

A STUDY OF THE MECHANISM OF CHEMICAL REACTIVITY  
OF NITROGEN TETROXIDE WITH TITANIUM ALLOYS

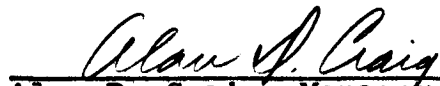
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Foreword

This is the second quarterly technical report prepared by the Research Center, Hercules Incorporated, under Contract No. NAS8-21207, Control No. DCN 1-7-54-20173 (1F) covering the period from October 1 through December 31, 1967. This report was prepared for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Propulsion and Vehicle Engineering Laboratory, Materials Division of the George C. Marshall Space Flight Center with Mr. W. A. Riehl acting as project manager. The sixth Monthly Progress Report has been integrated into this report. Scientific personnel currently participating in this program include:

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ABSTRACT

Phase A - Development of a Standard Corrosion Test

The development of a standard corrosion test procedure is essentially complete. In recent tests, 30 out of 30 U-bend specimens of 6 Al-4V titanium alloy cracked during exposure to Red Reactive (RR)  $N_2O_4$ , while no cracking was observed in 10 U-bend specimens exposed to Green 8 (0.8% NO)  $N_2O_4$  under identical conditions.

These results were obtained in four separate tests utilizing 10 specimens each and were carried out at 167°F. for a maximum of 72 hours. Twenty specimens formed with a radius 5 times the thickness broke in half after exposure to RR  $N_2O_4$  at a stress level of about 90% of the transverse or longitudinal yield strength. Another group of 5 pairs of specimens exposed to RR  $N_2O_4$  at stress levels of 30, 50, 70, 90 and 100+% of the longitudinal yield strength also cracked in less than 72 hours. A group of 10 specimens stressed to about 90% of the longitudinal yield strength and exposed to G8  $N_2O_4$  for 72 hours at 167°F. showed no evidence of cracking. This latter result will be confirmed with U-bend specimens formed transversely to the sheet-rolling direction.

The development of an all glass-Teflon test cell has not yet been accomplished. Current tests are being performed in glass pipe cells with Teflon end closures but with small stainless steel inlet and outlet valves. In view of the test results described above, the total elimination of potential sources of metal contamination may not be necessary.

Plans are under way for the preparation of Red Non-reactive (RN), Red Purified (RP), and Green 4 (G4)  $N_2O_4$ . These three materials will be prepared from the two types of  $N_2O_4$  currently on hand. Program efficiency may be improved by the performance of critical level addition experiments with NO and  $H_2O$  before preparing the RN and RP materials.

#### Phase B - Characterization of Propellant $N_2O_4$

During the past three months the analytical development effort under Phase B has been accelerated and expanded. Complete and applicable procedures are now available for the determination of total protonated species by nuclear magnetic resonance, trace metals content by emission spectrography and atomic absorption spectroscopy, and total chlorine by x-ray emission. The precision of the methods has been evaluated, and analyses of the bulk samples of RR and G8  $N_2O_4$  have been made. The methods also have been applied to  $N_2O_4$  from SCC tests, both before and after contact with the U-bend specimens.

Extension of the spectrophotometric method for the determination of nitric oxide down to the <50 ppm. NO level has not been achieved. Current evidence indicates that this analytical goal may not be realized because of unpredicted equilibrium changes that occur during the addition of small amounts of NO to an oxidized and degassed sample of  $N_2O_4$ . This apparent analytical setback may prove to be of positive value in reaching a better understanding of the critical equilibrium of the system.

Additional evaluation work has confirmed the fact that conventional mass spectrometry does not have adequate sensitivity and reliability for the determination of low levels of dissolved oxygen in liquid  $N_2O_4$ . Consequently, considerable effort has been devoted to the development of a gas chromatographic method for this purpose. Apparatus and calibration difficulties have limited progress and a completely acceptable method is not yet available.

Both NMR and visible spectrophotometry are providing increasing evidence for the presence of different species in RR and G8  $N_2O_4$ . For example, both the shape and the chemical shift of the proton peak are different in RR and G8 material. These phenomena will be extensively investigated during the next quarter, since the distribution of protonated species in various types of  $N_2O_4$  may well be a key factor in the mechanism of stress corrosion cracking.

TABLE OF CONTENTS

	<u>Page</u>
Abstract	2
Introduction	7
Phase A - Development of a Standard Corrosion Test	8
I. N <sub>2</sub> O <sub>4</sub> Test Material	8
II. Titanium Alloy Sheet	9
III. Lines and Piping	9
IV. Test Cell Development	9
V. Stress Corrosion Cracking Tests	11
VI. Stress Corrosion Cracking and Metal Dissolution	14
VII. Summary and Conclusions	16
VIII. Future Work	17
Phase B - Characterization of Propellant N <sub>2</sub> O <sub>4</sub>	19
I. Determination of Protonated Species by NMR Spectroscopy	19
II. Determination of Oxygen by Mass Spectroscopy	31
III. Determination of Oxygen by Gas Chromatography	34
IV. Determination of NO by Visible Spectroscopy	47
V. Determination of Dissolved Metals by Spectrochemical Analysis and Atomic Absorption Spectroscopy	53
VI. Determination of Chlorine by X-Ray Emission	67
VII. Revised Schedule of Analytical Effort	80
VIII. Bibliography	82

LIST OF FIGURES

	<u>Page</u>
Figure 1 - Line and Piping Arrangement	10
Figure 2 - Phase A - Development of a Standard Corrosion Test - Revised Schedule	18
Figure 3 - Variation of $\Delta$ H <sub>2</sub> O with % H <sub>2</sub> O for Various N <sub>2</sub> O <sub>4</sub> Samples	23
Figure 4 - Determination of Residual Water in NMR Sample Tubes	26
Figure 5 - NMR Spectra of 0.039% H <sub>2</sub> O in N <sub>2</sub> O <sub>4</sub>	29
Figure 6 - Gas Chromatogram of "RR" N <sub>2</sub> O <sub>4</sub>	35
Figure 7 - Gas Chromatogram of "G8" N <sub>2</sub> O <sub>4</sub>	37
Figure 8 - Calibration Curve for Oxygen in the Low Range	39
Figure 9 - Schematic of Apparatus Being Investigated for Determination of O <sub>2</sub> in N <sub>2</sub> O <sub>4</sub>	40
Figure 10 - Details of Sample Introduction System for Chromatography of N <sub>2</sub> O <sub>4</sub>	41
Figure 11 - Visible Spectra of NO in N <sub>2</sub> O <sub>4</sub> at Low Levels	49
Figure 12 - "Closed" Hydrolysis Schematic	56
Figure 13 - Cl Level Versus Counting Intensity Ratio - Extended Range	73
Figure 14 - Cl Level Versus Counting Intensity Ratio - Working Curve	74
Figure 15 - Specimen Preparation for Cl Analyses - Diagram of Mount	75
Figure 16 - Phase B - Characterization of Propellant N <sub>2</sub> O <sub>4</sub> - Revised Schedule	81

### INTRODUCTION

The specific objectives of this program are as follows:

(1) To develop a standard stress corrosion test capable of assessing the corrosive nature of various types of dinitrogen tetroxide ( $N_2O_4$ ) on 6 Al-4 V titanium alloy specimens.

(2) To develop methods of analysis capable of detecting and determining significant differences between various types of  $N_2O_4$ .

(3) To identify that constituent or component of  $N_2O_4$  which enhances or induces stress corrosion in 6 Al-4 V titanium alloy.

(4) To attempt to establish the possible presence of stress corrosion inhibitors in certain types of  $N_2O_4$  and to determine the concentration levels that are critical regarding their inhibitory action.

The work described in this report is primarily related to the achievement of the first two objectives. Progress toward the achievement of these goals is described in detail in the following sections.



Phase A. Development of a Standard Corrosion Test Procedure

I. N<sub>2</sub>O<sub>4</sub> Test Material

More complete analyses of the contents of the two 1-ton cylinders of N<sub>2</sub>O<sub>4</sub> (RR and G8) have been received from the producing plant in Hercules, California. These data are shown in Table 1. Additional discussion of several aspects of these values is included in the sections describing Phase B work.

Table 1

Composition of Red Reactive (RR) and Green 8 (G8) N<sub>2</sub>O<sub>4</sub> -  
Plant Analysis\*

<u>Analysis</u>	<u>RR (Cylinder No. 127) MIL-P-26539B</u>	<u>G8 (Cylinder No. 120) MSC-PPD-2A</u>
N <sub>2</sub> O <sub>4</sub> , %	99.99	99.26
NO, % (Colorimetric)	-	0.81; 0.86(1)
NO, % by MSC-PPD-2A	-	0.72
H <sub>2</sub> O, %	0.05	0.05
Cl as NOCl, %	0.001	0.001
CO <sub>2</sub> , %	0.028(2)	0.045(2)
O <sub>2</sub> , %	0.006(3)	0.002(3)
Particulate, mg./l.	2.3	3.1

(1) Obtained on last 10 grams of retained sample.

(2) Results are low because of inclusion of gas freezing. Actual % CO<sub>2</sub> could be 2 times the reported value.

(3) Argon is included in this test.

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\*Hercules Incorporated, Hercules, Calif. Certificate of Analysis dated Nov. 1, 1967 by W. J. Balling.

## II. Titanium Alloy Sheet

A 4' x 8' x 0.06" sheet of 6Al 4V ELI titanium alloy, mill annealed, and ground to a 240 grit finish is being used for the stress corrosion test development. Because of the possible relationship between the state of annealing and susceptibility to SCC, additional information was sought from the supplier (Titanium Metals Corporation). This sheet was taken from Heat No. G-4056 which was given a "car bottom" anneal for 8 hours at 1350°F. followed by an air cool. No special annealing furnace atmosphere was described so it is assumed to be air.

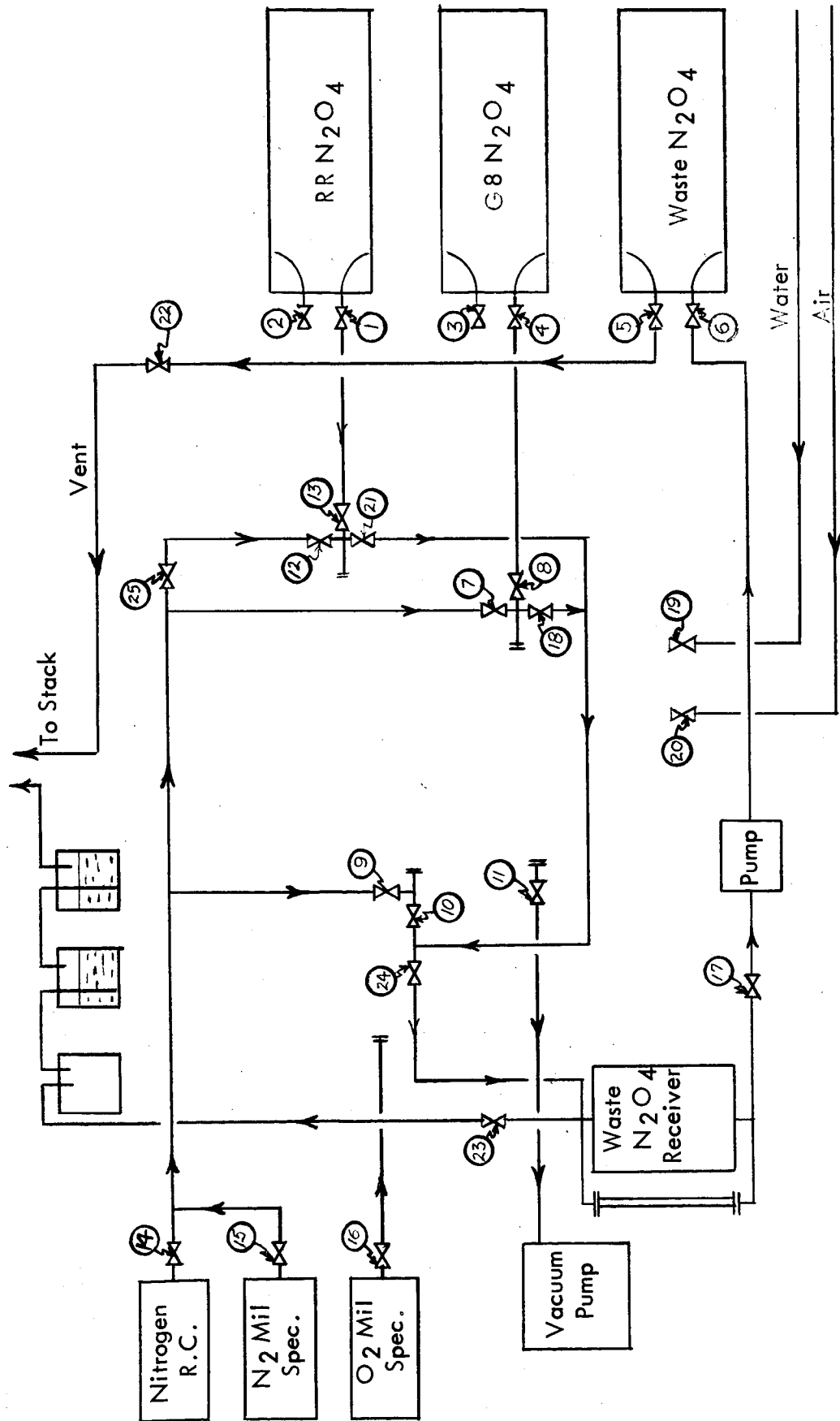
## III. Lines and Piping

Lines and piping associated with the test program have been changed to provide a smoother transfer of different types of  $N_2O_4$  into the test cells. Waste  $N_2O_4$  removal modifications have also been made. These changes are shown in Figure 1. The valve markings in the figure are referred to in the standard operating procedure used in  $N_2O_4$  handling.

## IV. Test Cell Development

The development of a leak-free test cell in which the  $N_2O_4$  contacts nothing but glass or Teflon has proven to be more difficult than anticipated. Numerous problems involving end closure leakage, slippage of Teflon-glass and Teflon-Teflon connections, and valve fragility have prevented the attainment of this goal within reasonable time and cost limits. In order to maintain progress in the program, reasonable compromises have been effected. Initial

FIGURE 1  
LINE AND PIPING ARRANGEMENT NASA  $N_2O_4$  STUDY



stress corrosion tests, that will be described in the following sections, were performed using 304 stainless steel end closures. These closures were detectably etched by the RR  $\text{N}_2\text{O}_4$  but not by the G8 material.

An improved compromise design involves the machining of a solid 3-5/8" diameter cylinder of Teflon to produce what is essentially a 3" pipe to 3/8" tubing reducer. This closure is a 3-9/16" diameter, 3/8" thick disk of Teflon with an off-center protrusion 1-13/16" long and 3/8" diameter. This integral length of tubing fits through a hole in a cast iron, back-up flange which is bolted to the test cell and produces a leak-free closure. Standard tubing fittings or valves with tubing fittings can be attached to the protruding tubing. Thus far, only stainless steel tubing fittings and valves have given satisfactory performance. One successful stress corrosion test run has been made in this unit. Attempts to attach an all-Teflon valve or a Fischer-Porter glass-Teflon valve are continuing. However, additional successful tests in the unit with the stainless steel valve may well indicate that an entirely Teflon-glass system is unnecessary and that exposure to the small metal surface of the valve is not a critical factor.

#### V. Stress Corrosion Cracking Tests

Three SCC tests have been made with Red Reactive  $\text{N}_2\text{O}_4$  and one with G8 (0.8% NO) material. As indicated in the previous section, two of the RR tests and the G8 test were carried out in

test cells with 304 stainless steel end closures. The third RR test was carried out in the cell with the modified Teflon closures. The results of these tests are summarized in Table 2. In the three SCC runs with RR  $N_2O_4$ , 30 out of 30 U-bend specimens were cracked in less than 70 hours at the test temperature (167°F.). None of the specimens exposed to the G8  $N_2O_4$  under the same conditions showed any cracks. The 80-fold reduction of the exposed stainless steel surface between runs 1 and 3 did not significantly affect the results.

The specimens that failed had multiple cracks on each U-bend and generally one major crack that broke the specimen in half. Twenty-six of the 30 failed specimens cracked through at the geometric center. U-bends loaded to nominal stress levels of 30% and 50% of the yield strength (139,000 psi.) had major cracks near the juncture between the radial and straight portions of the pre-bend. At the lowest stress level, the major crack did not propagate all the way across the 3/4" wide U-bend. The single non-cracking run made with G8  $N_2O_4$  used specimens bent parallel to the rolling direction. An identical run will be made with bends made transverse to the rolling direction.

Table 2

Standard Stress Corrosion Cracking Test Results

Stress Cracking Run No.	N <sub>2</sub> O <sub>4</sub> Type	Failure Rate	Failure Descript.	Bend Orientation (Respect to Rolling Direction)	Stress Level, Nominal % of Yield Strength	Exp. Time, Hours	Test Temp. °F.	Test Conditions	Remarks
1-1	RR	10/10	∅ of U-bend (many cracks)	parallel	90	68.5	167	304 Stainless Steel End Closure, S.S. area to N <sub>2</sub> O <sub>4</sub> Vol., 0.11 cm. <sup>2</sup> /cm. <sup>3</sup>	
1-2	RR	10/10	"	transverse	90	69	167	Same as above	
2	G8 (0.80% NO)	0/10	no cracks	parallel	90	72	167- 168	Same as above	
3	RR	2/2	∅ of U-bend (many cracks)	parallel	100+	70	167	Teflon End Closure & 304 SS Valve. Stain- less Steel surface area to N <sub>2</sub> O <sub>4</sub> Vol., 0.0014 cm. <sup>2</sup> /cm. <sup>3</sup>	
		2/2	"	"	90				
		2/2	"	"	70				
		2/2	Tangent area (many cracks)	"	50				
		2/2	Many cracks, U-bend still one piece	"	30				

## VI. Stress Corrosion Cracking and Metal Dissolution

The RR and G8  $N_2O_4$  samples used in the SCC test runs were analyzed for metals content by atomic absorption and emission spectroscopy. Samples of Run Nos. 1-2 and 2 (Table 2), in which stainless steel end closures were used, were concentrated approximately 5-fold by room temperature evaporation in a platinum crucible. The concentrated samples were then hydrolyzed and analyzed. The results are shown in Table 3.

These data revealed an increase in the iron, titanium, vanadium, and aluminum content of the RR  $N_2O_4$  after the SCC test run. Only a slight increase in iron content was observed in the G8  $N_2O_4$  after the test run. Either the RR  $N_2O_4$  is more generally corrosive than the G8  $N_2O_4$ , or metal dissolution occurred at the numerous cracks that were generated during the RR test run. Unstressed or unloaded U-bends could be used to determine the corrosion rate in both types of  $N_2O_4$ . If a value of 1 mil/year is found for RR  $N_2O_4$ , then solution at the cracks may be small enough to be neglected. Speculation on the possible number of cracks and atom layers dissolved from either surface of the crack suggests that 25 atom layers are involved with 10,000 cracks to produce a concentration of 25 ppm. titanium in the  $N_2O_4$ .

Table 3

Metal Present in Red Reactive (RR) and  
Green 8 (G8) N<sub>2</sub>O<sub>4</sub> Before and After Exposure to  
Ti 6Al 4V ELI Alloy U-bends. (Runs 1-2 & 2)

<u>N<sub>2</sub>O<sub>4</sub> Type</u>	<u>Chemical Element, ppm. (Atomic Absorption)</u>						
	<u>Fe</u>	<u>Cr</u>	<u>Ni</u>	<u>Al</u>	<u>Ti</u>	<u>V</u>	
Red Reactive (RR)							
Pre-Exposure	0.33	<0.03	<0.03	<0.33	<0.65	<0.13	
Post Exposure	1.3	0.03	<0.03	0.42	25.5	9.0	
Green 8 (G8, 0.80% NO)							
Pre-Exposure	1.1	<0.03	<0.03	<0.33	<0.65	<0.13	
Post Exposure	1.6	<0.03	<0.03	<0.33	<0.65	<0.13	
<u>N<sub>2</sub>O<sub>4</sub> Type</u>	<u>Chemical Element, ppm. (Emission Spectroscopy)</u>						
	<u>Mg</u>	<u>Mn</u>	<u>Pb</u>	<u>Si</u>	<u>Ca</u>	<u>Cu</u>	<u>Zn</u>
Red Reactive (RR)							
Pre-Exposure	<0.06	<0.03	<0.01	0.1	0.06	0.006	<0.1
Post Exposure				<0.1	<0.06		
Green 8 (G8)							
Pre-Exposure	<0.06	<0.03	0.01	0.1	<0.06	0.006	<0.1
Post Exposure			<0.01				
<u>N<sub>2</sub>O<sub>4</sub> Type</u>	<u>Chemical Element, ppm. (Emission Spectroscopy)</u>						
	<u>Na</u>	<u>Sn</u>	<u>Bi</u>	<u>Sb</u>	<u>Cd</u>	<u>B</u>	<u>Co</u>
Red Reactive (RR)							
Pre-Exposure	<1	<0.02	<0.1	<0.1	<0.1	<0.1	<0.1
Post Exposure							
Green 8 (G8)							
Pre-Exposure	<1	<0.02	<0.1	<0.1	<0.1	<0.1	<0.1
Post Exposure							



Some apparent anomalies are noted in the data. Iron increased from 0.33 to 1.3 ppm., presumably from corrosion of the stainless steel end closures. However, chromium and nickel values did not show a corresponding rise. An increase in titanium content from <0.65 to 25.5 ppm. was accompanied by a disproportionate rise in vanadium content, <0.13 to 9.0 ppm., but with only a slight increase in Al level, <0.33 to 0.42 ppm. A completely satisfactory explanation of these results has not yet been developed, although selective attack by  $N_2O_4$  and/or possible losses of volatile metal species during concentration may be involved.

#### VII. Summary and Conclusions

Although numerous difficulties have been encountered, progress has been made toward the development of an all glass-Teflon test cell. The latest design incorporates a Teflon disk end-closure machined to include a length of 3/8" O.D. Teflon tubing as an integral part of the closure. Only small stainless steel needle valves presently contribute any exposed metal surface. A further attempt to incorporate non-metallic valves will be made, but additional SCC testing may prove that this is unnecessary.

Titanium alloy U-bends exposed to RR  $N_2O_4$  at 167°F. have failed 30 out of 30 times in less than 72 hours during three separate runs. Twenty of the specimens were stressed at approximately 90% of the yield strength while 10 other specimens were stressed between 30 and 100+%. A single exposure of 10 U-bend specimens to G8  $N_2O_4$  under identical conditions (167°F., 90% of yield strength) resulted

in completely crack-free specimens. Another run with G8  $N_2O_4$  in a cell with Teflon end closures is expected to confirm that a standard test procedure has been developed.

The metals content of RR  $N_2O_4$  increased in Fe, Ti, V, and Al levels during an SCC test in a cell with stainless steel end closures. No discernible change in the concentration of these metals was observed when G8  $N_2O_4$  was used in the same test procedure. A higher degree of general corrosivity of the RR  $N_2O_4$  may be involved or an increased rate of attack at the fresh surfaces exposed by the many cracks in the specimens.

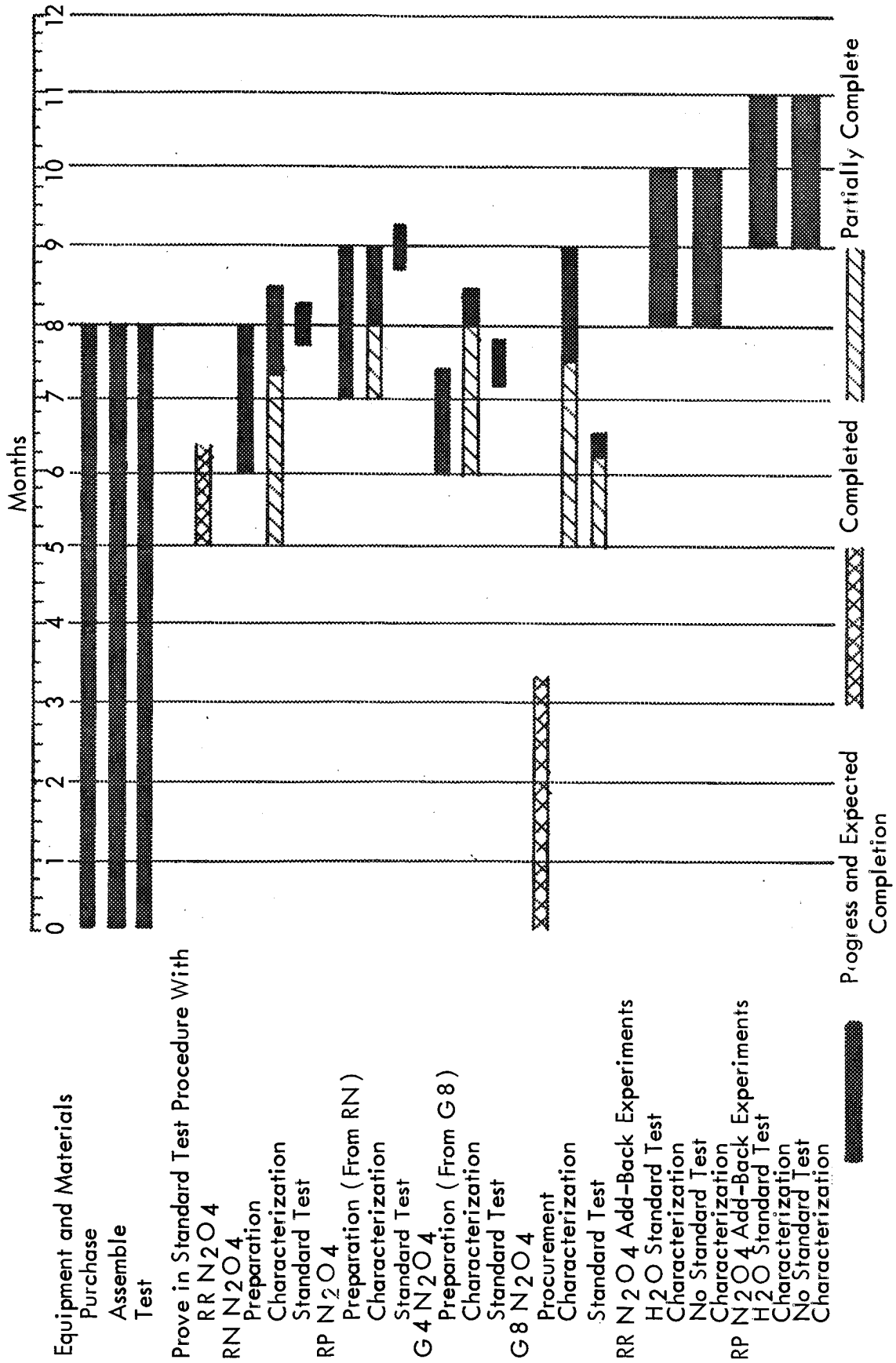
#### VIII. Future Work

Additional SCC tests will be made using the cell with Teflon end closures. Tests will also be run with unstressed specimens to compare the general corrosivity of RR and G8  $N_2O_4$ .

The preparation of G4 (0.4% NO)  $N_2O_4$  from G8 material will be begun and the preparation of the so-called Red Non-Reactive (RN) and Red Purified (RP)  $N_2O_4$  will be attempted.

Controlled add-back experiments to establish the minimum quantities of  $H_2O$  and NO that must be added to RR  $N_2O_4$  to prevent stress corrosion cracking will be initiated.

FIGURE 2  
PHASE A DEVELOPMENT OF A STANDARD TEST PROCEDURE  
REVISED SCHEDULE



## Phase B. Characterization of Propellant $N_2O_4$

### I. Determination of Protonated Species by NMR Spectroscopy

#### A. Introduction

In the previous quarterly report, preliminary work aimed at developing an improved procedure for the determination of water in  $N_2O_4$  using nuclear magnetic resonance (NMR) spectroscopy, was described. The improved procedure differs from one previously described in the literature (1) in that an internal standard is added to the  $N_2O_4$  to provide a peak area/concentration calibration factor (K), rather than basing the calibration on the addition of known amounts of water to a series of aliquots of the unknown sample. In addition to greatly simplifying the analysis, the internal standard method may provide a more accurate analysis due to an effect which has come to our attention since the writing of our last report. In a recent publication, Saraf and Fatt (2) describe a variation in the sensitivity of NMR detection of  $H_2O$  in a variety of liquid systems. Normally, the area of an NMR peak is assumed to vary linearly with the concentration of absorbing protons in the sample, and a K factor calculated for a known sample may be used as a calibration for the analysis of an unknown sample of similar composition. Saraf and Fatt, however, showed that K varied with the ionic conductivity of the sample. This effect was shown to be due to a variation of the quality factor, Q, of the sample detector coil with the conductivity of the sample, and can cause a significant error in the determination of water in samples

which are chemically similar but differ in conductivity. This is of importance in the present work, since the conductivity of  $\text{H}_2\text{O}$ -containing  $\text{N}_2\text{O}_4$  samples varies with the water content. Thus, a series of samples of increasing water content such as were used in the previously described NMR method (1) for  $\text{H}_2\text{O}$  in  $\text{N}_2\text{O}_4$ , would be expected to have a varying K. For this reason, when a plot of peak area vs. % added water is prepared, the extrapolation to zero added water would not give an accurate value for the amount of water originally in the sample.

This problem is avoided in the present internal standard procedure since, in a given sample, the Q factor will be the same for the  $\text{H}_2\text{O}$  and internal standard peaks, and the area/concentration factor will therefore be the same for both peaks.

During the second quarter, effects of experimental variables such as sample temperature, water concentration, and type of  $\text{N}_2\text{O}_4$  studied on the NMR spectra of the sample were studied, and a detailed study of the accuracy and precision limits of the method were carried out. This work is described in the present report.

## B. Discussion of Results

### 1) Spectral Characteristics of the $\text{N}_2\text{O}_4$ - $\text{H}_2\text{O}$ System

In our previous quarterly report, it was pointed out that the chemical shift of the water peak in  $\text{N}_2\text{O}_4$  ( $\delta_{\text{H}_2\text{O}}$ ) varies with the water concentration, due to a shift in the equilibrium between  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$ , and any other protonated species participating in the exchange of the hydrogen ions in the system. In order to

determine if this phenomenon could be used as the basis for a quantitative analysis for  $\text{H}_2\text{O}$ , the effect of various experimental conditions on the chemical shift difference between the  $\text{H}_2\text{O}$  and benzene interval standard peaks ( $\Delta_{\text{H}_2\text{O}}$ ) was carried out.

First, an important difference between the spectral characteristics of "red" and "green" samples of  $\text{N}_2\text{O}_4$  was noted. Samples of the bulk tank samples of red (RR) and green (G8)  $\text{N}_2\text{O}_4$ , which were found to contain approximately the same amount of water ( $0.090 \pm .01\%$ ) were observed to give distinctly different peak shapes for the  $\text{H}_2\text{O}$  peak. In analyzing a number of aliquots of both samples, the red  $\text{N}_2\text{O}_4$  was always observed to give a relatively sharp, narrow peak, with a line width at half-height ( $\nu_{1/2}$ ) of  $\approx 2$  Hz. The green  $\text{N}_2\text{O}_4$ , however, gave a broad, poorly defined peak, with  $\nu_{1/2}$  in the range of 8-12 Hz. This would suggest that the species participating in the equilibrium reaction which gives rise to the so-called "water peak" in  $\text{N}_2\text{O}_4$  are exchanging much more rapidly in the red  $\text{N}_2\text{O}_4$  than the green. When additional water is added to the samples, the peak in the green sample becomes narrower and at  $>0.2\%$   $\text{H}_2\text{O}$  is similar to that observed in red  $\text{N}_2\text{O}_4$ . In both samples  $\Delta_{\text{H}_2\text{O}}$  decreases or  $\text{C}_{\text{H}_2\text{O}}$  increases (the peaks shift to higher field).

The effect of sample temperature on  $\Delta_{\text{H}_2\text{O}}$  in red and green  $\text{N}_2\text{O}_4$  is shown by the data given in Table 4. The effect of temperature on  $\Delta_{\text{H}_2\text{O}}$  is quite different for the two samples. In red  $\text{N}_2\text{O}_4$ , the  $\text{H}_2\text{O}$  peak shifts slightly to lower field as T decreases. In green  $\text{N}_2\text{O}_4$ ,

Table 4

Effect of Sample Temperature (T) on  
the Chemical Shift of H<sub>2</sub>O ( $\Delta$  H<sub>2</sub>O) in N<sub>2</sub>O<sub>4</sub>  
(Both samples contain 0.09  $\pm$  0.01% H<sub>2</sub>O)

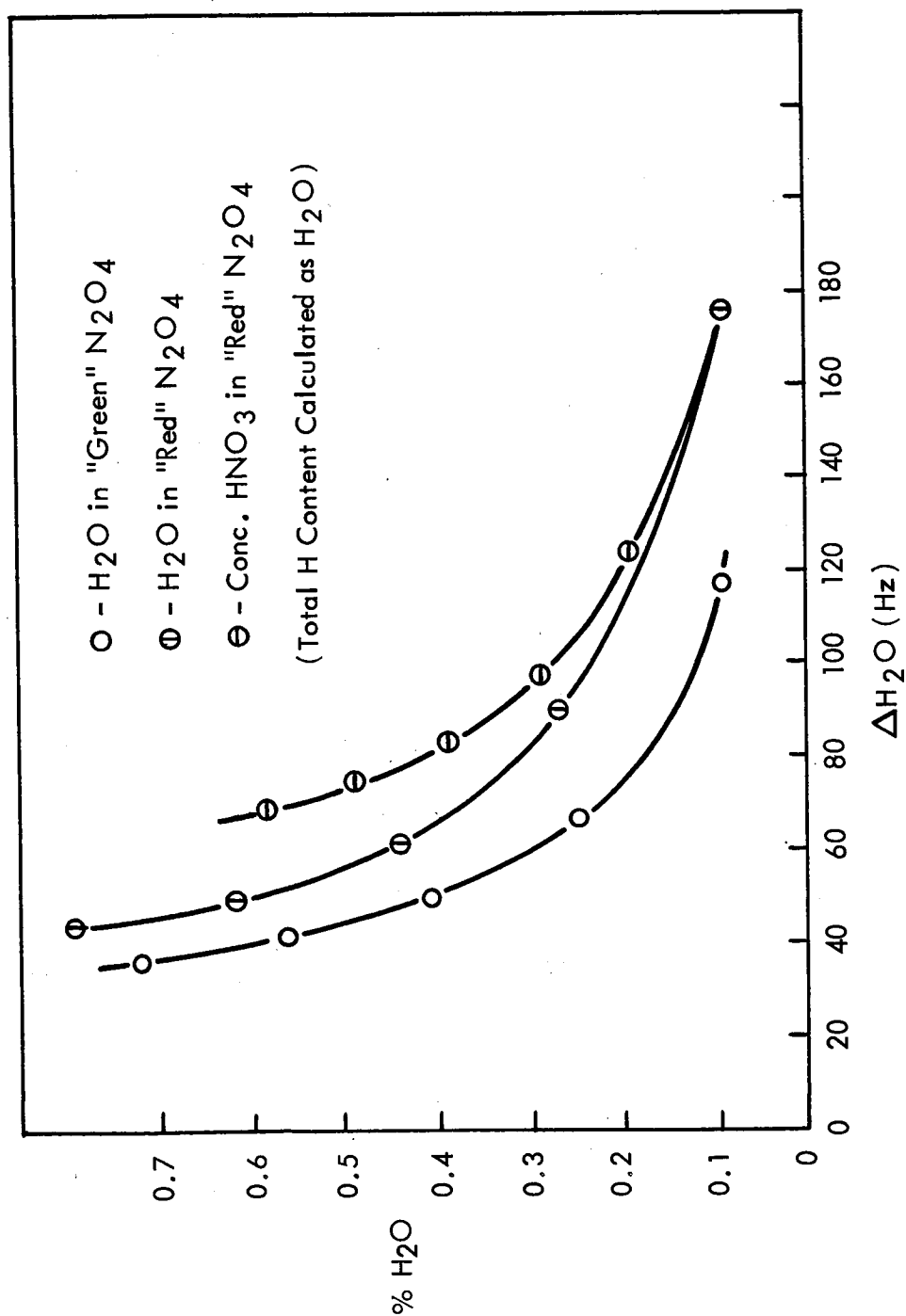
T (°C.)	$\Delta$ H <sub>2</sub> O (Hz)	
	Red N <sub>2</sub> O <sub>4</sub>	Green N <sub>2</sub> O <sub>4</sub>
+23.2	204	160
+12.0	206	146
+ 0.5	206	133
- 7.5	210	113

the H<sub>2</sub>O peak shifts to higher field as T decreases, with a temperature coefficient for the shift 5-10 times larger than observed in red N<sub>2</sub>O<sub>4</sub>.

These results suggest that the use of  $\Delta$  H<sub>2</sub>O as a measure of the H<sub>2</sub>O concentration in N<sub>2</sub>O<sub>4</sub> is not practical, since  $\Delta$  H<sub>2</sub>O and its temperature dependence, is markedly different for different N<sub>2</sub>O<sub>4</sub> samples. This is to be expected, since the observed "water peak" is actually the average peak due to several equilibrating protonated species, and the chemical shift of the average peak will vary with the relative concentrations of the equilibrating species. An example of the effect of sample composition on  $\Delta$  H<sub>2</sub>O is shown in Figure 3, in which plots of  $\Delta$  H<sub>2</sub>O vs. the total proton concentration, calculated as % H<sub>2</sub>O, are given for three different systems. It is obvious from this data that  $\Delta$  H<sub>2</sub>O is not a good

FIGURE 3

VARIATION OF  $\Delta H_2O$  WITH %  $H_2O$  FOR  
VARIOUS  $N_2O_4$  SAMPLES





measure of %  $\text{H}_2\text{O}$  for an unknown sample. On the other hand, the chemical shift of the water peak in  $\text{N}_2\text{O}_4$ , as well as its width and the nature of the temperature dependence of its chemical shift may be useful in determining the nature of the protonated species in  $\text{N}_2\text{O}_4$ . This will be investigated in the future.

## 2) Quantitative Studies

In order to complete development of the quantitative aspects of the NMR method for  $\text{H}_2\text{O}$  in  $\text{N}_2\text{O}_4$ , several studies of the precision and accuracy of the method were carried out.

Since the amount of water in a typical two-gram sample of  $\text{N}_2\text{O}_4$  containing 0.1%  $\text{H}_2\text{O}$  is only 2.0 mg., the water adsorbed on the surface of the NMR sample tubes may contribute significantly to the amount determined in an unknown sample. In order to determine the amount of water contributed to the sample by the sample tubes and sampling system, an experiment was carried out in which aliquots of the same sample, varying in size from 0.9 to 2.2 g. were analyzed in typical sample tubes. The total amount of water found in the sample,  $(\text{H}_2\text{O})_{\text{obs.}}$ , is equal to the amount contributed by the sampling system and sample tube,  $(\text{H}_2\text{O})_{\text{T}}$ , plus the amount contributed by the sample,  $(\text{H}_2\text{O})_{\text{S}}$ . Since  $(\text{H}_2\text{O})_{\text{S}}$  is proportional to the sample size, we may write:

$$(\text{H}_2\text{O})_{\text{obs.}} = (\text{H}_2\text{O})_{\text{T}} + W_{\text{S}}C_{\text{S}}$$

where  $W_{\text{S}}$  is the sample weight and  $C_{\text{S}}$  is the water concentration in the sample. Since  $(\text{H}_2\text{O})_{\text{T}}$  and  $C_{\text{S}}$  are constant, a plot of  $(\text{H}_2\text{O})_{\text{obs.}}$  vs.  $W_{\text{S}}$  has an intercept at  $W_{\text{S}} = 0$  equal to  $(\text{H}_2\text{O})_{\text{T}}$ . The results of such

an experiment are shown in Figure 4. The experimental points plotted are the average of four integrals for each sample. The line was obtained by linear regression analysis of the data, and has an intercept of 0.04 mg. Statistical analysis of the data gives an upper limit, at the 95% confidence level, of 0.19 mg. of water contributed to the observed water concentration by the sample tube and sampling system. This corresponds to 0.01% in a typical two-gram  $\text{N}_2\text{O}_4$  sample.

The accuracy of the method, and the validity of the basic assumption that the calibration factor,  $K$ , is the same for the benzene and water peaks under our experimental conditions was tested by add-back experiments. When 0.250%  $\text{H}_2\text{O}$  was added to three two-gram samples of  $\text{N}_2\text{O}_4$  whose original  $\text{H}_2\text{O}$  content had previously been determined, the amounts of added water found by the NMR procedure were 0.246% ( $S = 0.013$ ), 0.260% ( $S = 0.007$ ), and 0.248% ( $S = 0.007$ ). These data confirm the accuracy of the procedure, within the limit of the precision obtainable at this level.

The precision of the NMR procedure has been determined by replicate analysis of several samples containing 0.03 to 0.2%  $\text{H}_2\text{O}$ , and the results of this work are summarized in Table 5. The only measured quantities used in calculating these results are the sample weight, which can be determined to  $\pm 1$  mg. for a two-gram sample, the amount of internal standard added, which is measured to  $\pm 2\%$ , and the measured area of the NMR peak. The latter appears to be the principle source of error, as evidenced by the variance data in Table 5.

FIGURE 4  
DETERMINATION OF RESIDUAL WATER IN NMR SAMPLE TUBES

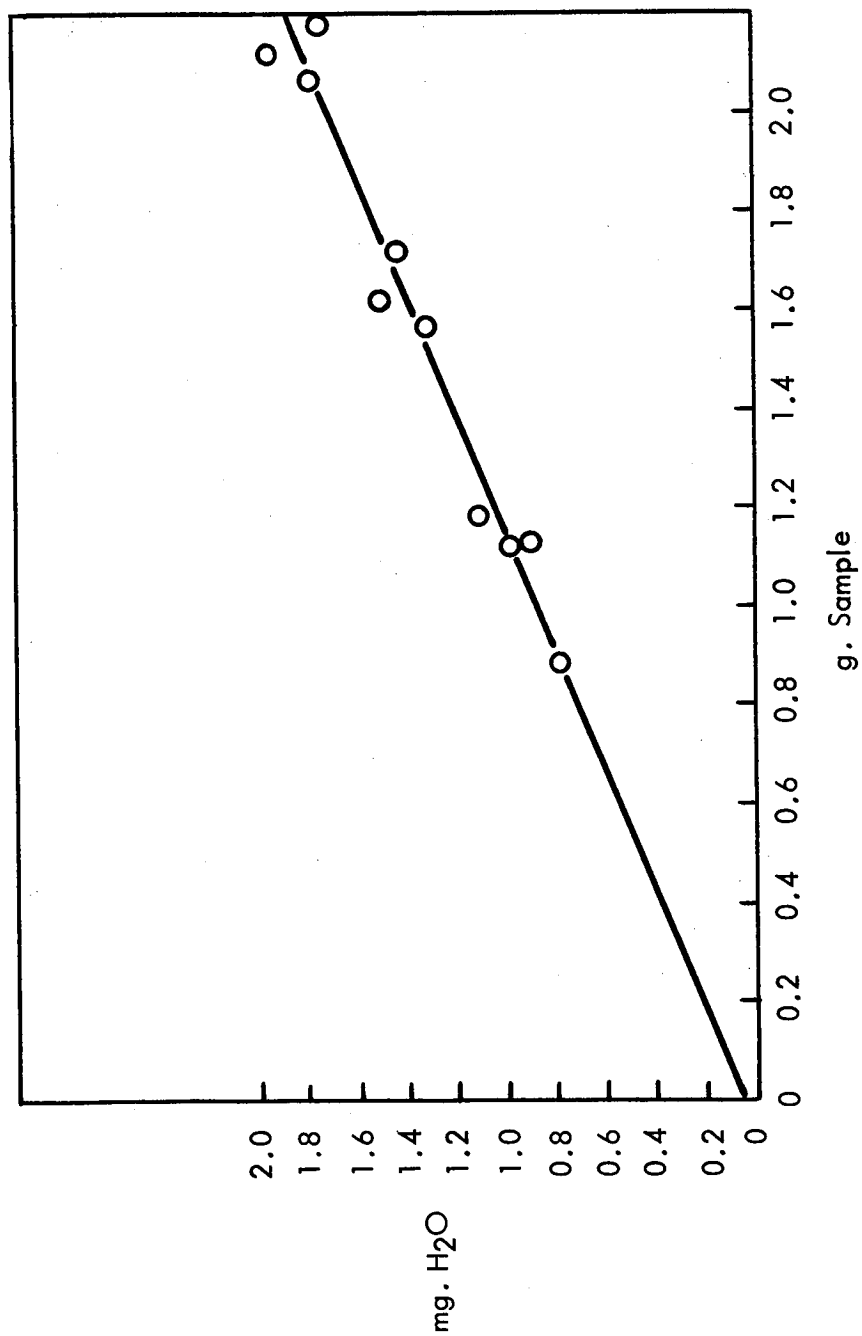


Table 5

<u>N<sub>2</sub>O<sub>4</sub> Sample</u>	<u>Individual Replicate Analyses</u>		<u>Overall Averages</u>	
	<u>% H<sub>2</sub>O*</u>	<u>S*</u>	<u>% H<sub>2</sub>O**</u>	<u>S**</u>
Matheson N <sub>2</sub> O <sub>4</sub>	0.195	0.017	0.195	0.002
	0.198	0.024		
	0.194	0.012		
	0.192	0.012		
Hercules "RR" N <sub>2</sub> O <sub>4</sub>	0.095	0.006	0.088	0.006
	0.080	0.006		
	0.087	0.002		
	0.089	0.005		
Hercules "G8" N <sub>2</sub> O <sub>4</sub>	0.097	0.005	0.090	0.017
	0.069	0.009		
	0.094	0.010		
	0.101	0.018		
Laboratory Distilled N <sub>2</sub> O <sub>4</sub>	0.0359	0.0033	0.0351	0.0026
	0.0312	0.0037		
	0.0371	0.0027		
	0.0360	0.0037		

\*Calculated from four integral scans of same sample.

\*\*Calculated from Individual Replicate Analyses.

Time averaging of the spectrum, which increases the signal-to-noise ratio, should thus result in a more precise analysis. In order to demonstrate this improvement, and to prove that the limit of detection of the method can be extended to the 0.01%  $\text{H}_2\text{O}$  level, a sample found to contain 0.0360%  $\text{H}_2\text{O}$  by the single scan method ( $S = 0.0037$ ), was re-analyzed using a time-averaged spectrum obtained by summing fifty scans of the sample. In this experiment, the benzene peak was used to trigger the repetitive scan, and a smaller amount of nitrobenzene was added as an internal standard. Typical single scan and time-averaged spectra are shown in Figure 5. The time-averaged data gave %  $\text{H}_2\text{O} = 0.0393$  with  $S = 0.0007$ , or a relative standard deviation of 1.8%. The signal-to-noise level of the time-averaged spectrum in Figure 5 is obviously high enough to permit reliable detection, if not measurement, of 0.01% water, since a peak one-fourth as high as the observed one would still give a signal-to-noise ratio of nearly four to one.

This spectrum was obtained using a sweep time of 100 sec., so that the analysis time, including sample preparation and calculation is increased to nearly two hours, with approximately 90 minutes of spectrometer time required for each run.

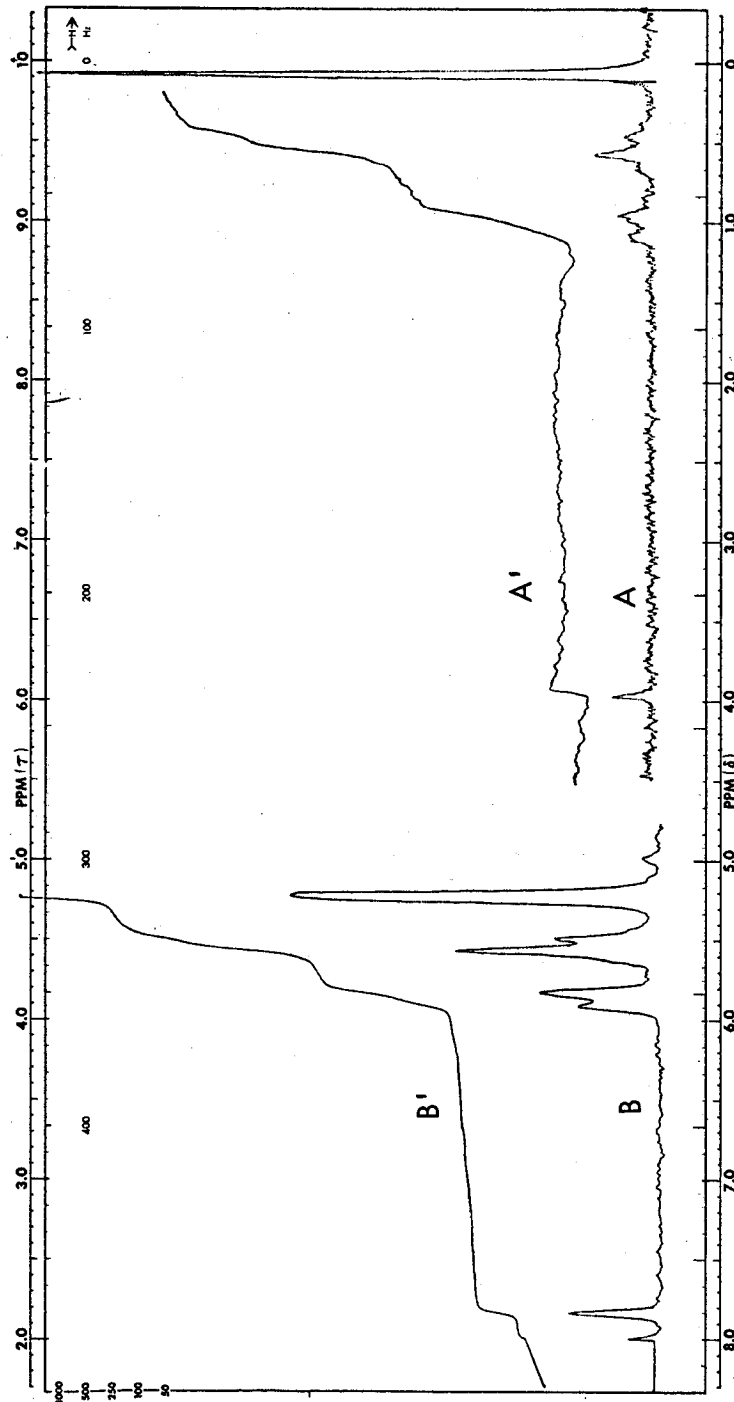
### C. Conclusions

The results presented in the previous section show that our present NMR method for the determination of water in  $\text{N}_2\text{O}_4$  is reliable and practical for use in the analysis of samples containing 0.05%  $\text{H}_2\text{O}$  or more. At this level a relative standard

FIGURE 5

NMR SPECTRUM OF 0.039% H<sub>2</sub>O IN N<sub>2</sub>O<sub>4</sub>

- Curve A - Single Scan
- Curve A' - Integral of A
- Curve B - Time Average of 50 Scans
- Curve B' - Integral of B



60 MHz NMR  
Spectrum No.: 1906  
Operator: G. A. Ward  
Date: December 5, 1967  
Sample: X 16078-16

(A)  
Solvent: None  
Temperature: 10°C.  
Filter Bandwidth: 1 Hz  
R.F. Field: .02 mG  
Sweep Time: 250 sec.  
Sweep Offset: --  
Spectrum Amp.: 40  
Integral Amp.: 40  
Remarks:

(B) = Time Average of  
50 Scans of A.  
Sweep Time = 100 sec.  
Scan Width = 300 Hz  
Read Out in 100 sec.,  
with ST = 250

deviation in the range 5-10% is obtained for results calculated from integration of a single NMR scan. The precision of the method can be significantly improved by time-averaging the NMR spectrum to improve the signal-to-noise ratio, at a cost of additional spectrometer time per run.

Since the present sample handling system was found to contribute  $\leq 0.01\%$   $\text{H}_2\text{O}$  to a typical two-gram sample, the procedure would have to be modified to obtain valid data at the  $0.01\%$   $\text{H}_2\text{O}$  level. Principally, oven-drying of the sample tubes and handling system and filling of sample tubes in a dry  $\text{N}_2$ -flushed glove box would be necessary.

Our bulk samples of both RR and G8  $\text{N}_2\text{O}_4$  have been analyzed and found to contain  $0.09 \pm 0.01\%$   $\text{H}_2\text{O}$ . Since this represents the lowest concentration level at which the method must be used in the corrosion study at present, no further refinement of the analysis will be attempted immediately.

#### D. Future Work

In the next quarter we will attempt to determine whether the NMR method can be used to determine the distribution of protons among the various species contributing to the equilibrium system in  $\text{N}_2\text{O}_4$ .

## II. Determination of Oxygen by Mass Spectrometry

### A. Introduction

During the first quarter most of our effort was spent on studying the means of obtaining consistent mass patterns at all of the peaks observed in the  $N_2O_4$  spectrum. This involved the study of preconditioning procedures and preparing purified materials which were either NO or  $O_2$  free. The mode of sampling liquid  $N_2O_4$  was also investigated and volatilization of a small quantity of liquid  $N_2O_4$  directly into the instrument inlet was chosen. It was hoped that mass spectrometry would provide a rapid sensitive method for the determination of oxygen. However, interference from the  $N^{18}O^+$  ion and  $O_2$  formed by the reaction  $N_2O_4 \rightleftharpoons 2 NO + O_2$  yield such a large peak at  $m/e = 32$  that the degree of uncertainty limits the level of detection and the accuracy of the determination. Consequently mass spectrometry efforts in the second quarter were minimized while the potentially more sensitive gas chromatographic method was investigated. The efforts expended on mass spectrometry were aimed at establishing the sensitivity limits of the method.

### B. Discussion of Results

#### 1) Detection of $O_2$ by Use of Large Sample

In order to magnify any differences that exist between G8 ( $N_2O_4$  containing 0.8% NO) and RR (red-reactive  $N_2O_4$ ) a larger sampling stem of 5  $\mu$ l. volume was used in the Micro Tek sampling valve. This gives a peak height of about 8000 divisions at  $m/e = 30$ .



Each sample was run 4 times and the ratio of  $m/e = 32$  to  $m/e = 30$  was obtained. G8 gave a percent ratio of 1.46% with  $S = 0.035$  and RR gave 1.55% and  $S = 0.024$ . If the average value is assumed to be the true ratio and using the measured sample pressure it is calculated that RR contains 0.025% (weight) of oxygen. However, it should be noted that the difference between the two ratios is just slightly greater than their standard deviations so the significance of the calculated value is highly questionable.

2) Determination of Oxygen Using the Ratio  
 $m/e = 32$  to  $m/e = 31$

It was felt that it might be possible to determine the oxygen content of the  $N_2O_4$  samples from the ratio of the peaks at  $m/e = 32$  to  $m/e = 31$  in both RR and G8 plus the measured sample pressure. To increase the peak height the ionizing current was increased five-fold from 20 to 100  $\mu A$ . To insure resolution on the galvanometer recording, the scan speed was slowed such that traversing the interval from  $m/e = 26$  to  $m/e = 36$  took about 50 seconds. This represents a voltage scan from 1500 to 1100 volts which was used for this experiment.

Operating under the above conditions it was found that more exhaustive conditioning was necessary. The particular need seemed to be located in the sampling valve and mass spectrometer inlet.

A sample of G8 was run 4 times and gave an average ratio of 7.3065 with  $S = 0.0114$  which was used as the background correction. If it is assumed that a difference would have to be

greater than 3S for accurate measurement, then the limit of detection of  $O_2$  calculated from this one set of samplings is 0.0051% (weight).

Four samplings were then made of RR. The ratio for the first sampling was out of line with the other three so it was ignored and assumed to have been contaminated. The oxygen content was calculated for the other samplings and gave values for the weight percent of oxygen as 0.0146, 0.0146 and 0.0075% respectively.

#### C. Conclusions

Mass spectrometry is not suitable for detection of  $O_2$  in  $N_2O_4$  at low levels. The detection limit is in the 50 ppm. range. Measurements have been made at the 100-200 ppm. level but with very poor precision and unproven accuracy.

#### D. Future Work

No further development work with the mass spectrometric method is immediately contemplated.

### III. Determination of Oxygen by Gas Chromatography

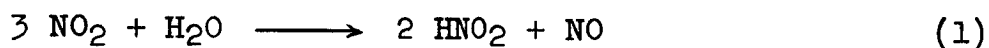
#### A. Introduction

The mass spectrometric determination of oxygen in  $N_2O_4$  has been shown to have a limit of detection of about 50 ppm. Previous work (3) on a gas chromatographic method showed a more likely avenue of success at lower oxygen concentrations.

#### B. Discussion of Result

An apparatus, similar to that described by Conner and Ward (3) was assembled. A stainless trap and an aluminum valve with a Teflon core was substituted for the glass U-tube trap and the Teflon three-way valve used in the previous work. Also, a 1-foot by 1/4-inch O.D. U-tube column packed with 0.5% Carbowax 1000 or 70 mesh glass beads was inserted in the train.

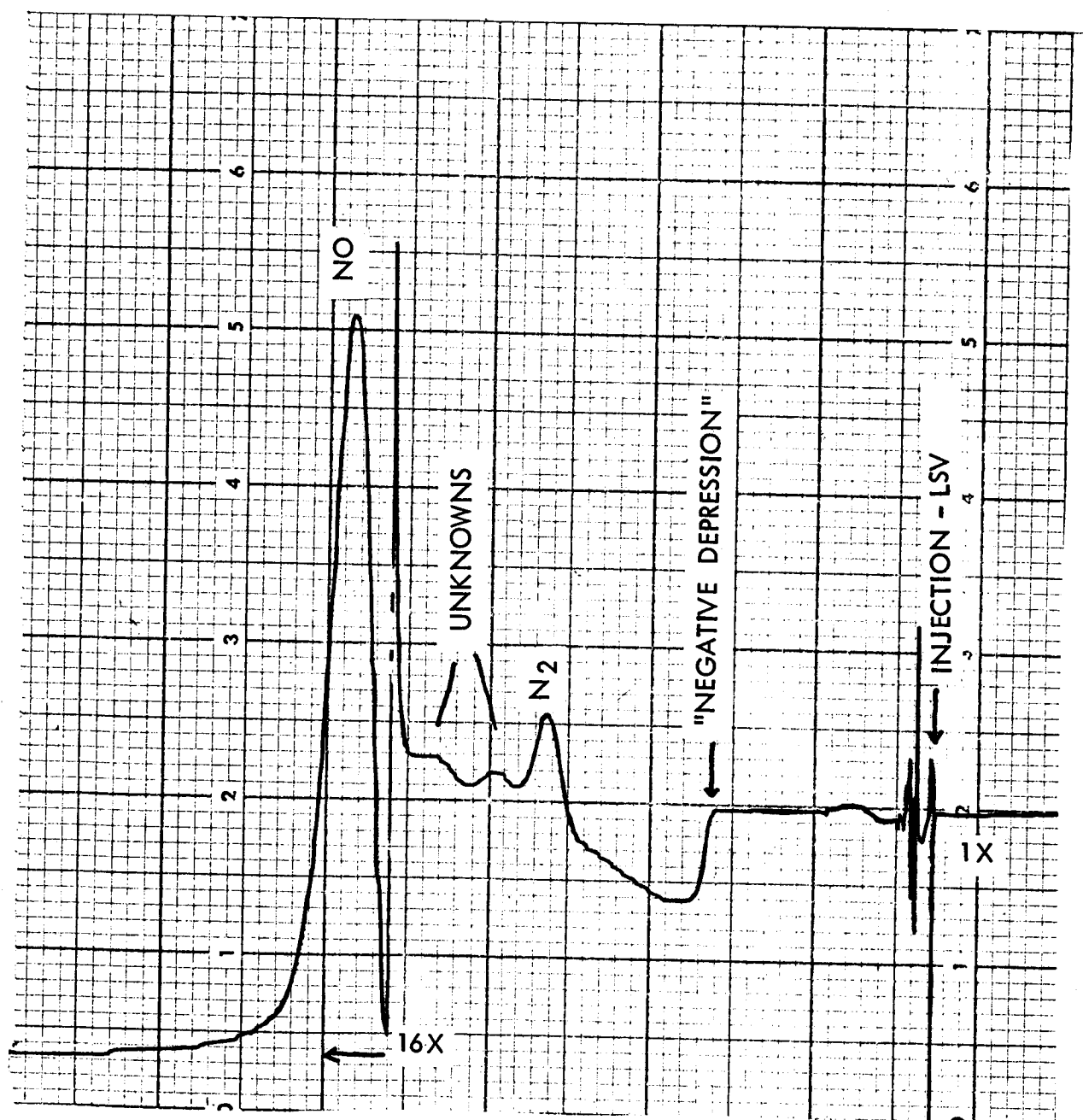
It was soon discovered that the precolumn of Carbowax 1000 produced complications which were apparently due to the presence of water associated with the column packing. Thus, the reactions



could occur. Reaction 2 could be responsible for the negative depression in the gas chromatogram baseline in the area of the oxygen peak (see Figure 6 as an example), when samples of both NO deficient or "Red" (RR, Mil-P-26539A) and NO rich or "Green" (G8, MSC-PPD-2A)  $N_2O_4$  were run.

FIGURE 6

GAS CHROMATOGRAM OF "RED"  $\text{N}_2\text{O}_4$  (RR, MIL-P-26539A)  
30 MICROLITERS; TEMPERATURE =  $24.2^\circ\text{C}$ .



Removal of the precolumn eliminated the negative baseline depression for the "Red"  $\text{N}_2\text{O}_4$  but it persisted for the "Green" material. Typical runs of the Red and the Green are shown in Figures 6 and 7 respectively. The presence of the negative depression is typical of reactions in situ, but the exact cause has not, as yet, been determined. The nitrogen peak (Figures 6 and 7) was observed to be of varied size which might be caused by an air leak around the liquid sampling valve stem. Thus reaction 2 could proceed in the case of NO rich  $\text{N}_2\text{O}_4$ .

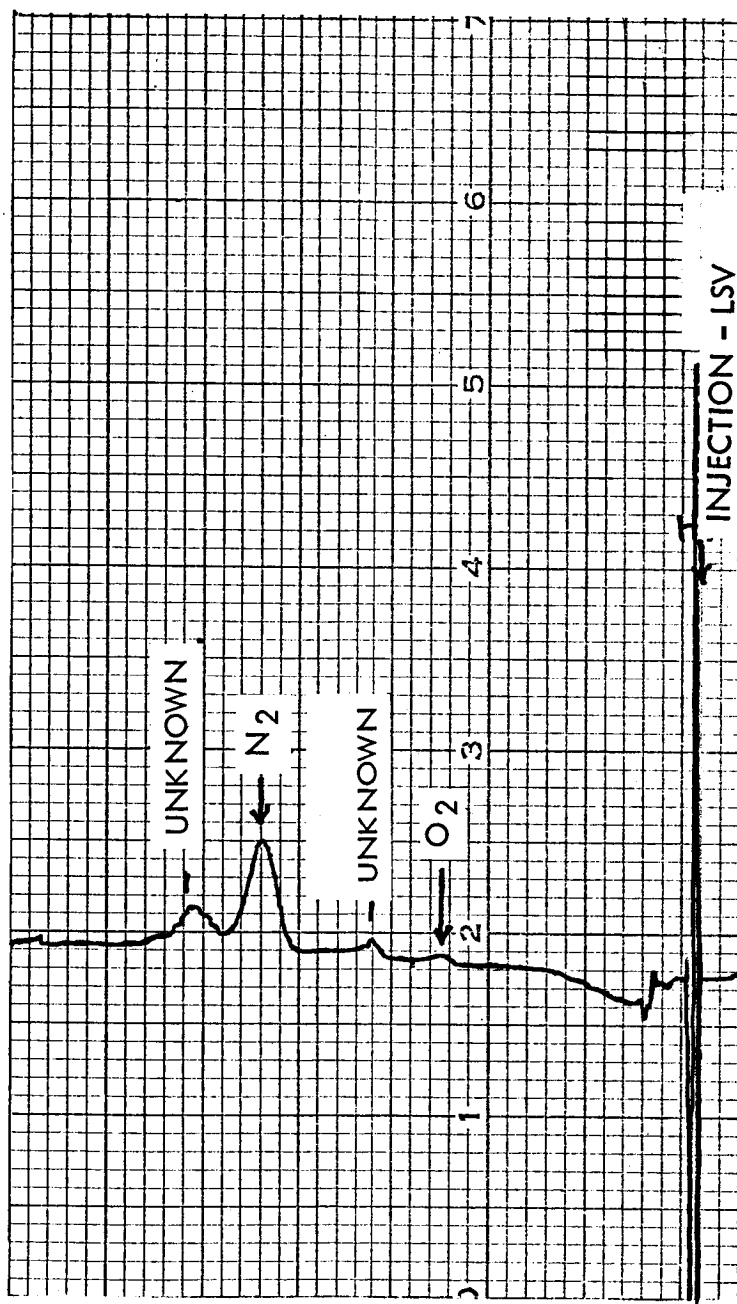
Neither straightening of the stem nor replacement of the stem and "O"-rings cured the problem; a nitrogen peak of varied size (no detectable oxygen) was still observed when the liquid sampling valve (LSV) chamber was flushed with helium and the atmosphere sampled by working the valve.

To circumvent possible leaks in the valve, an apparatus has been constructed which may allow elimination of the LSV. The equipment is shown in Figure 9. The "glove bag" should provide an essentially oxygen-free atmosphere. Also, an accurate measure of sample size (via syringe) at a uniform temperature should be possible.

A 1' x 1/4" O.D. SS precolumn packed with hydrophobic Porapak Q, conditioned at 150°C. for 12 hours, was also installed in the line to again attempt the preliminary separation of NO,  $\text{O}_2$  and  $\text{N}_2$  from  $\text{N}_2\text{O}_4$ .

FIGURE 7

GAS CHROMATOGRAM OF "GREEN"  $\text{N}_2\text{O}_4$  (G8, MSC-PPD-2A)  
30 MICROLITERS; TEMPERATURE =  $25^\circ\text{C}$ .



### Calibration for Oxygen

Initial attempts to calibrate for oxygen determination in a liquid were made by air-saturating various liquids in which the solubility of oxygen is known. Such a compilation is available from Seidell (4), in which is given the Ostwald coefficients, 1, or the volume of gas absorbed by a volume of liquid at any temperature and pressure. The data are given in Table 6. Also included are the calculated concentrations of oxygen in parts per million when the source of oxygen is air or

$$\text{ppm. O}_2 = \frac{1 \times 32 \times 0.2099 \times 10^6}{2.241 \times 10^4 \times d} = \frac{1}{d} \times 2.997 \times 10^2 \quad (3)$$

where d is the density of the liquid. Since the changes are small in converting specific gravity to density, the values for the specific gravity as given in Lange's Handbook of Chemistry (5) were assumed applicable and constant over the temperature range given in Table 6.

The data given in Table 6 is limited in range and hence, calibration was made by chromatographing known amounts of air. The air was injected via syringe through a septum fitted on the "T" (no glove bag attached) as shown in Figure 10.

A plot of area of the oxygen peak versus micrograms of oxygen injected is shown in Figure 8 for the low oxygen range (0 to 1.5 micrograms oxygen or 0 to 34.5 ppm. for a 30 microliter sample). A plot over the range of 0 to 7.5 micrograms of oxygen

FIGURE 8  
CALIBRATION FOR OXYGEN IN THE LOW RANGE  
(0.075 - 1.5 MICROGRAMS)

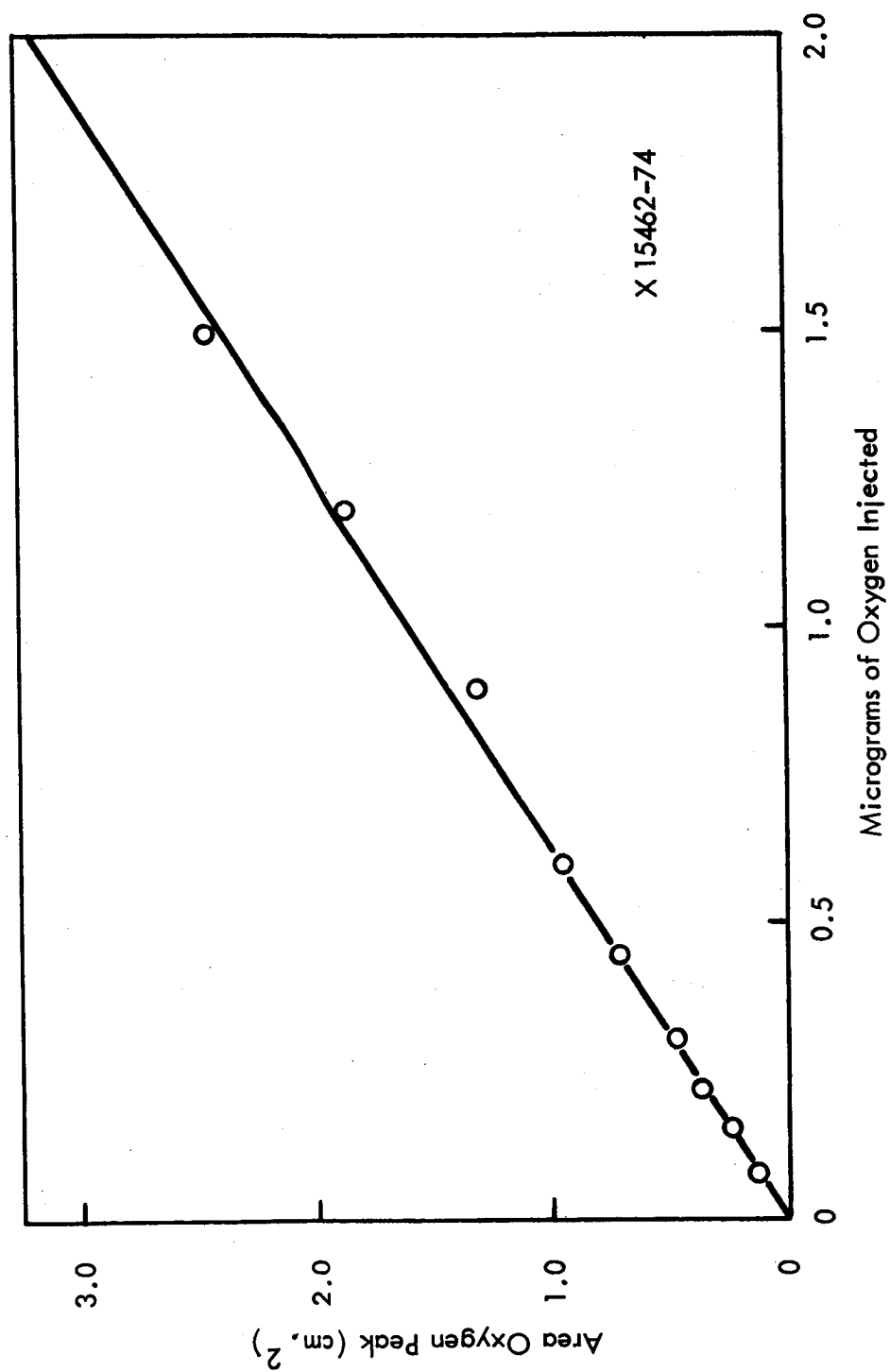
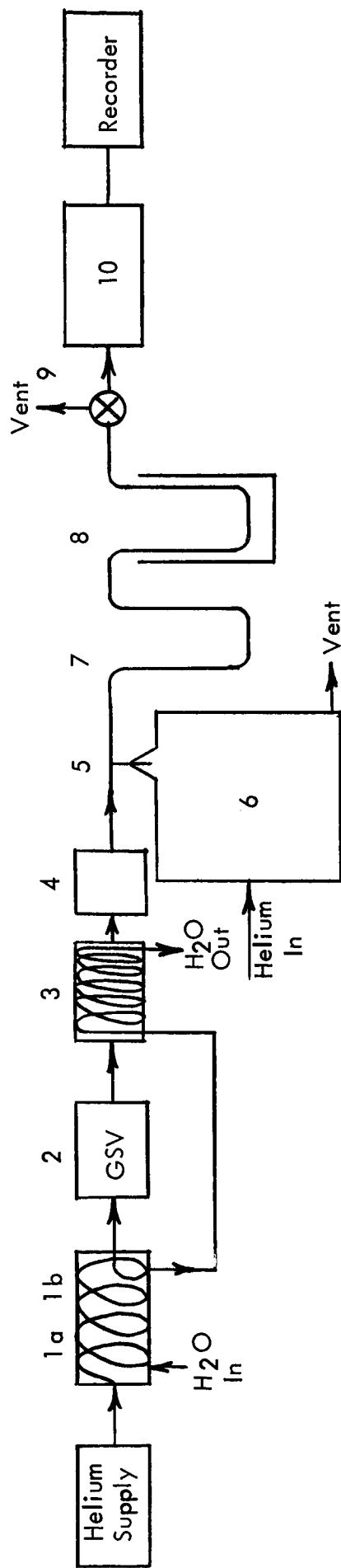




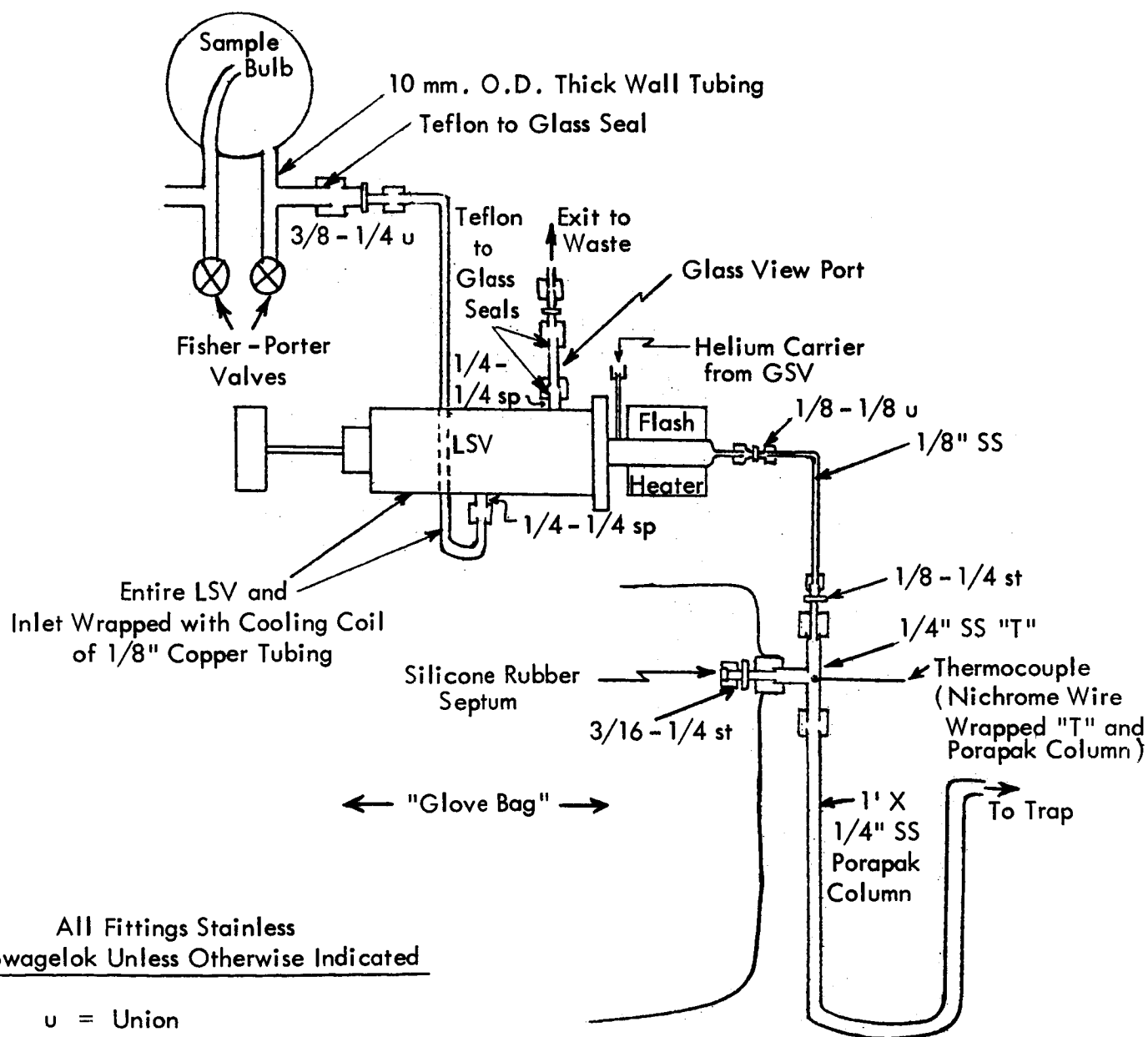
FIGURE 9  
SCHEMATIC OF G.C. APPARATUS FOR DETERMINATION OF O<sub>2</sub> IN N<sub>2</sub>O<sub>4</sub>



1. Wet Ice Bath with
  - a) 12' X 3/8" O.D. Cu. Tube Packed with HA Molecular Sieve Activated at 300°C. for 24 Hours.
  - b) Coils for Cooling Water for Cooling of the Liquid Sampling Valve.
2. Gas Sampling Valve (GSV) - Perkin-Elmer Rotary GSV, Cat. No. 1540067.
3. Liquid Sampling Valve (LSV) - Microtek Valve No. 1502, 30 Microliter Capacity.
4. Heated Microtek Inlet
5. 1/4" Swagelok "T" Fitted with Rubber Septum and Nichrome Wire Heater.
6. "Glove Bag" Fitted Over Swagelok "T" and Containing Samples and Necessary Accessory Equipment.
7. 1' X 1/4" O.D. SS Tube Packed with Porapak Q and Wrapped with Nichrome Wire Heater.
8. 1' X 1/4" O.D. SS Tube Trap Held at -78°C. and Wrapped with Nichrome Wire Heater.
9. Three-Way Aluminum and Teflon Valve
10. 12' X 1/4" O.D. SS Tube Packed with 13X Molecular Sieve Activated for 4 Hours at 300°C. (52.9 Grams)

FIGURE 10

DETAIL OF ARRANGEMENT FOR INTRODUCTION OF  $N_2O_4$   
INTO GAS CHROMATOGRAPH



All Fittings Stainless  
Swagelok Unless Otherwise Indicated

u = Union

st = Swagelok to Tubing

sp = Swagelok to Pipe

SS = Stainless Steel

is also linear and passes through the origin. An average percent relative standard deviation of 5.9% was observed over the entire range. A calibration factor of  $0.632 \pm 0.047 \mu\text{g./cm.}^2$  was calculated.

The lowest point on Figure 8 is represented by 0.25 microliters of air or 0.075 micrograms of oxygen. This is about the limit of sensitivity of the method. Based on a 30 microliter sample of  $\text{N}_2\text{O}_4$  the limit of accurate oxygen determination in  $\text{N}_2\text{O}_4$  is calculated to be about 2 ppm. A limit of detection of 1 ppm. is possible. The limit of detection could probably be improved if the glove bag apparatus proves successful since, in this case, the sample size is not limited to 30 microliters.

From the data in Figure 8, the amounts of oxygen in the various liquids chromatographed were calculated and compared to the literature values (Table 7). Except for one set of three determinations on carbon tetrachloride there appears to be little or no difference between the method of injection (LSV versus syringe). There does appear to be some correlation between recovery of oxygen and the volatility of the solvent. This may be related to the ability of the precolumn to separate air from the liquid in question at 60-70°C. Hence, as the liquid plus partially resolved air enters the cold trap some redissolution of oxygen may occur. In future work this will be checked by monitoring the solvent-air separation.

The validity of the 100% recovery of oxygen from  $\text{CCl}_4$  when samples were taken inside the glove bag must also be checked. At this time instrumental problems arose which cast some doubt on these results.

#### C. Future Work

When instrumental problems have been overcome, the reason for low recoveries of oxygen from various liquids must be checked. Valid results for  $\text{N}_2\text{O}_4$  cannot be expected if a determination on knowns cannot be made. Knowns will also include  $\text{N}_2\text{O}_4$  which will be saturated with oxygen from air. Further research into the cause of the negative baseline depression for "Green"  $\text{N}_2\text{O}_4$  must also be made.

#### D. Experimental

No set experimental procedure has as yet been developed. However, the following operating conditions have been established to some degree.

Carrier gas - Helium at 40 ml./min.

Molecular Sieve

Column Temp. - Ambient; 24-30°C.

Precolumn Temp. - 60-70°C.

LSV Flash Heater

Temperature - 60-70°C.

Cold Trap Temp. - -78°C. - Raise to 150°C. after each run.

The apparatus now in use is shown in Figure 9. Details of the various sample introduction systems are shown in Figure 10. These configurations are by no means firm. It should be noted that

when the LSV is used for sampling  $N_2O_4$ , the valve, as well as the inlet plumbing, must be cooled to avoid boil-off of  $N_2O_4$  as it runs through the system. To insure sufficient cooling of the  $N_2O_4$ , the sample must be slowly introduced into the valve. No bubbles should be seen in the viewport installed after the sampling chamber.

Table 6

Ostwald Coefficient, l, and Concentration of Oxygen(a) from Air in Various Liquids

Temp. °C.	CCl <sub>4</sub>		Chlorobenzene		Benzene		Acetone		Methyl Acetate		Ethyl Ether	
	l.	ppm.	l.	ppm.	l.	ppm.	l.	ppm.	l.	ppm.	l.	ppm.
-20	-	-	-	-	-	-	-	-	-	-	0.4247	179.8
0	0.2825	53.9	0.1748	47.3	-	-	0.2550	96.6	0.2488	75.1	0.4325	183.1
10	0.2926	55.0	0.1804	48.9	0.2091	71.3	0.2649	100.4	0.2583	78.0	-	-
20	0.2996	56.3	0.1863	50.5	0.2186	74.5	0.2736	103.7	0.2703	81.6	0.4511	191.0
25	0.3020	56.8	0.1890	51.2	0.2230	76.0	0.2800	106.1	0.2730	82.4	0.4550	192.6
30	0.3056	57.4	0.1915	51.9	0.2281	77.8	0.2846	107.9	0.2789	84.2	-	-
40	0.3124	58.7	0.1974	53.5	0.2371	80.8	0.2954	112.0	0.2877	86.8	-	-

From Reference 4

a) From Equation 3

Table 7

Experimental Versus Calculated Values for the Determination of Oxygen in Various Liquids

Liquid	Density	Temperature Range °C.(a)	No. of Determi- nations	ppm. O <sub>2</sub>		Average Percent Recovery	Percent Relative Standard Deviation
				Theoretical (Table 1)	Found (Avg.)		
CCl <sub>4</sub> (b)	1.594 20°/4°	24.5-24.9	5	56.8 (25°C.)	48.7	84.2	4.0
CCl <sub>4</sub> (c)	1.594 20°/4°	26.4-27.0	6	56.8 (25°C.)	43.6	76.7	4.1
CCl <sub>4</sub> (d)	1.594 20°/4°	29.3	5	57.4 (30°C.)	44.7	77.9	4.1
CCl <sub>4</sub> (e)	1.594 20°/4°	24.2	3	56.8 (25°C.)	56.8	100.0	-
Acetone(b)	0.791 20°/4°	23.4-24.4	5	106.12 (25°C.)	84.3	79.4	2.9
Acetone(c)	0.791 20°/4°	25.3-27.2	7	106.12 (25°C.)	75.3	71.0	3.1
Acetone(d)	0.791 20°/4°	29.3	2	107.9 (30°C.)	76.3	70.7	-
Ethyl Ether(b)	0.708 25°/4°	20.2-20.5	5	191.0 (20°C.)	87.9	46.0	2.0

a) Temperature of liquid during sampling.

b) Air introduced by bubbling air through the liquid immediately before sampling.

c) Equilibrated with air by stirring liquid.

d) As with c, except sample injected via syringe in air atmosphere.

e) Liquid sampled via syringe but in a helium atmosphere liquid sealed in tube with air atmosphere.

#### IV. Determination of NO by Visible Spectroscopy

##### A. Introduction

Measurement of the visible absorption band of  $N_2O_3$  peaking at 700 m $\mu$  has been shown to be the most accurate and convenient measure of NO in  $N_2O_4$  devised for the  $>0.1\%$  level (6). It was hoped that the lower limit of detection might be substantially reduced by 1) using low temperatures to reduce background absorption of  $NO_2$  2) using a longer photometric path length and 3) using an expanded scale slide wire on the spectrophotometer. The latter two changes give a potential fifty-fold increase in sensitivity.

During the first quarter most of the equipment was procured and/or fabricated and installed. The current quarter was spent attempting to achieve and prove-in the hoped for sensitivity increase.

##### B. Discussion of Results

###### 1) Cell Modification

Before work had progressed very far, it became evident that some modification to the cell would be needed. The cell in use had the sample entry and exit ports located at "3 and 9 o'clock". With this cell, not only was sample handling difficult, but contraction of the sample on cooling left a bubble in the light path. Fabrication of a cell with "bottom to top" ports rather than "side to side" ports not only made filling the cell easier, but the overhead exit port chamber contains sufficient sample reserve to permit contraction of the sample on cooling without forming a bubble in the light path.



With the decrease in temperature from about  $3^{\circ}\text{C}$ . to  $-10^{\circ}\text{C}$ . in the current version of the method, and the increase in sensitivity of this work compared to the original, cell window fogging became much more of a problem. Attempts to eliminate the fogging by purging the cell compartment and by directing jets of dry air at the windows required such a large volume flow that temperature control was adversely affected. The problem was completely eliminated by the additions of plexiglas "storm windows" to the outside of each cell window. These were in the form of 1/2-inch thick plexiglas collars with thin plexiglas windows and small ports in the collar to permit a minimal flow of by gas between the cell window and the "storm window". With the low gas flow, the desired temperature can be much more quickly attained and more easily maintained.

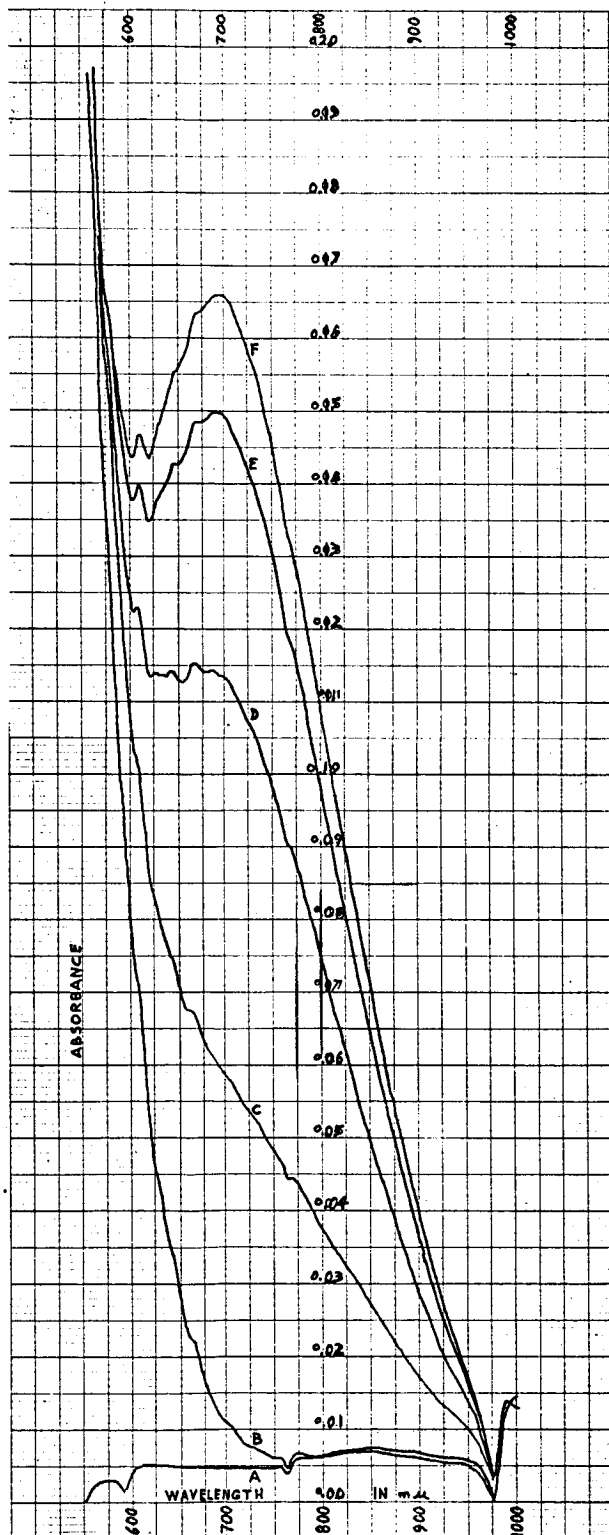
With the increased sensitivity from the cell, slide wire and cryostat our first concern was that the background absorption of the  $\text{NO}_2$  in NO-free  $\text{N}_2\text{O}_4$  might be a major interference. A number of runs of NO-free  $\text{N}_2\text{O}_4$  have shown that this is not the case; that a small and quite reproducible absorbance difference in the order of 0.0050 to 0.0100 absorbance units between 900 and 700  $\text{m}\mu$  is obtained (Figure 11).

## 2) NO Standards

With the mechanical difficulties eliminated and the reproducibility of the NO-free  $\text{N}_2\text{O}_4$  spectrum proven, the next step was to calibrate through the use of samples of  $\text{N}_2\text{O}_4$  with known concentrations of NO.

NO IN N<sub>2</sub>O<sub>4</sub>, CARY 14 USING NIR DETECTOR AND SOURCE  
SPECIAL CELL COOLED TO -10°C., PATH LENGTH 1 CM.

Curve	p.p.m. by wt. NO in N <sub>2</sub> O <sub>4</sub>
A	Cell Blank, CCl <sub>4</sub> in Cell
B	0
C	142
D	192
E	297
F	478



### Triphenyl Phosphine Procedure

It was hoped that these standard NO in  $N_2O_4$  samples might be easily prepared by the addition of triphenyl phosphine, reported to react with  $NO_2$  to give NO. The possibility of this becoming a convenient way of making known NO in  $N_2O_4$  samples was investigated. Samples were prepared by the addition of triphenyl phosphine to oxygen treated and subsequently degassed samples of  $N_2O_4$  and examined in the spectrophotometer. A high level addition (equivalent to 2500 ppm. NO) showed a 700  $m\mu$  band, but about 1/2 the expected intensity. Since calibration was running behind schedule, it was decided to drop, at least temporarily, the triphenyl phosphine approach and go with the proven vacuum line addition of NO to  $N_2O_4$  procedure.

### 3) NO Addition

A number of samples of  $N_2O_4$  containing 50 to somewhat less than 200 ppm. NO were prepared on the vacuum line by H. L. Young. These all exhibited an unexpected spectrum, a nonspecific general absorption increasing with decreasing wavelength but with no absorption maximum at 700  $m\mu$  (cf. Figure 11).

A number of experiments were undertaken to try to pinpoint the nature of this general absorption. Two stainless steel bombs were filled with RR  $N_2O_4$  from the large tank in order to have a convenient supply to make standards. Successive samplings from the bombs showed the same increasing background absorption noted above.

Five identical samples were withdrawn from the large tank of RR  $N_2O_4$ , examined and found to give clean, NO-free spectra. One of these was degassed only, a second had 200 ppm. NO added, a third had 500 ppm. NO added, a fourth had 1000 ppm. NO added and a fifth was retained as a hold sample. The degassed and hold samples gave normal NO-free spectra. The 1000 and 500 ppm. NO showed a definite band at 700  $m\mu$  but with evidence for the "general background" absorptives. The 200 ppm. NO sample showed only a shoulder at 700  $m\mu$  superimposed on the general background. An additional 100 ppm. NO was added to the 200 ppm. NO sample. The  $\Delta A$  700-900  $m\mu$  at the start was 0.0090 absorbance units; after the first 200 ppm. NO addition it was 0.0845 and after the further addition of 100 ppm., it was 0.1130 yielding  $\Delta A$  changes of 0.0755 and 0.0295 respectively. Obviously the change is not proportional to the NO added. The sample containing 500 ppm. NO was  $O_2$  treated and its spectrum was observed to revert to a typical NO-free spectrum. This indicates that the general absorption observed is not some foreign contaminant such as insoluble material, but some species which is formed upon the addition of NO and can be destroyed by addition of  $O_2$ . Unless a means can be found to eliminate this species or at least determine accurately how much of the total absorption it contributes, the limit of detection of NO may have to be raised from the hoped for 10-20 ppm. to 200 ppm. Until more is known about the nature of this absorbing species, quantitative measurement of NO as  $N_2O_3$  will be impossible from the lower limit of detection (about 200 ppm.) up to an as yet undetermined level where the interference is relatively insignificant.

C. Future Work

On the speculation that the interfering absorption may be related to a protonated species, we hope to prepare some water-free  $\text{N}_2\text{O}_4$  and repeat the NO addition experiments.

V. Determination of Dissolved Metals by Spectrochemical Analysis and Atomic Absorption Spectroscopy

A. Introduction

The primary purpose of this work is to determine the metallic contaminants of  $N_2O_4$  by Spectrochemical (Emission Spectrographic) and Atomic Absorption methods of analysis. Four methods of preparation of  $N_2O_4$  samples for analysis have been investigated; 1) controlled evaporation followed by hydrolysis, 2) direct aqueous hydrolysis in an open system, 3) hydrolysis in a closed system and 4) direct analysis of  $N_2O_4$ . These procedures are being intercompared as are analyses of  $N_2O_4$  samples before and after exposure of titanium alloy. Analyses of metallic contaminants are being used to help characterize the reactivity of  $N_2O_4$  with 6Al-4V alloy.

B. Discussion of Results

1) Sample Preparation Techniques

$N_2O_4$  has been prepared for analyses of trace metals by four routes; controlled evaporation followed by hydrolysis, 2) direct aqueous hydrolysis in an open system, 3) hydrolysis in a closed system and 4) direct analyses of  $N_2O_4$ . The first three methods have the advantage of concentrating the sample prior to analysis by either spectrochemical or atomic absorption methods thus enhancing the sensitivity of the analysis. The disadvantages of the hydrolysis or evaporation procedures is the need for blank corrections and the time consumed. Direct aspiration of  $N_2O_4$  into the atomic absorption spectrometer is unquestionably the fastest method, but

it sacrifices the sensitivity achieved by concentration. At the moment it may also suffer from our lack of knowledge about correction factors to be used or the spectral effects of  $N_2O_4$  in the flame background.

The evaporation and open hydrolysis techniques were compared on Matheson  $N_2O_4$  prior to receipt of the RR and G8 samples used in all subsequent work. Comparison of results by emission spectrography and atomic absorption spectroscopy on Matheson  $N_2O_4$  prepared by the two concentration techniques are given in Table 8 in the Experimental Section. Since the two concentration procedures give essentially the same results on metal contents with the major exceptions being those metals most likely leached from glass, the controlled evaporation procedure was used for most of the subsequent analyses. The data of Table 8 also demonstrate the capability of emission spectrography and/or atomic absorption spectroscopy to analyze many metals of interest in the fractional ppm. range in  $N_2O_4$ .

## 2) Metal Contents of Hercules "RR" and "G8" $N_2O_4$

A list of metals similar to those found in the Matheson samples were seen in the Hercules "RR" and "G8" samples upon arrival. Inspection of the spectrographic plate indicated that "RR" and "G8" differed significantly only in their iron contents. The results of atomic absorption analyses for iron and other significantly detected metals are given in Table 9. Replication of the evaporation and analysis steps established the levels and

precision of analyses. The results demonstrate that a significant difference in Fe content exists with the "G8" sample containing 0.83 ppm. S = 0.078 ppm. Fe and the "RR" sample containing 0.31 ppm. S = 0.013 ppm. Fe.

3) Metal Contents of "RR" and "G8" After Corrosion Testing

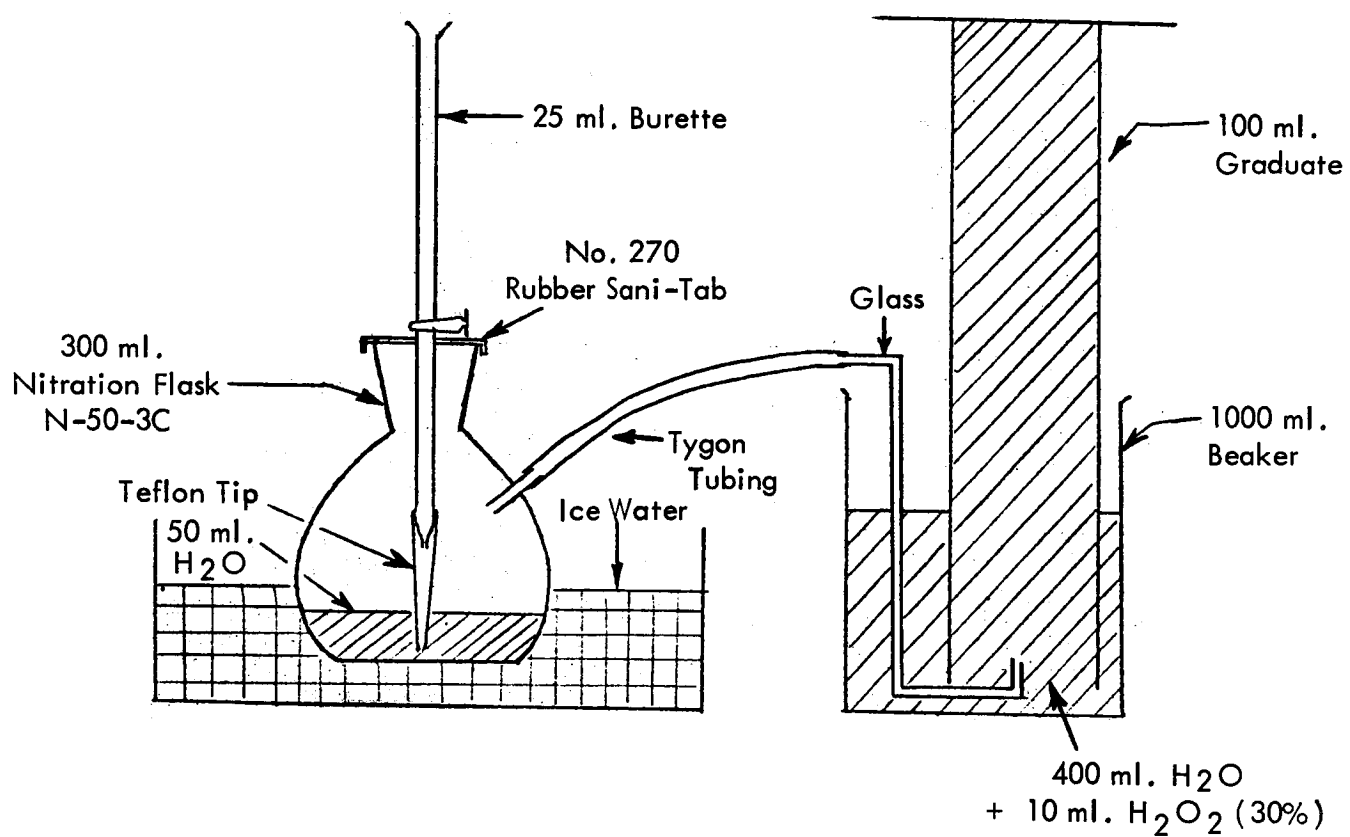
The data of Table 10 compare "RR" and "G8"  $N_2O_4$  for metal contents before and after 72-hour exposure in the corrosion test. The presence of stainless steel end plates in this test is noticeable in a slight increase in the Fe content of "G8"  $N_2O_4$  after exposure. No other metal content change in "G8" is exhibited. The marked increases in Ti, V and Al contents, the moderate increase in Fe content after exposure of "RR"  $N_2O_4$  indicates real differences in chemical reactivity between "green" and "red"  $N_2O_4$  as discussed in more detail in Part A of this report.

4) "Volatile" Metals in  $N_2O_4$

The possibility of volatile metal forms was tested using iron as the most likely candidate to exhibit volatile forms. Hydrolysis of a "G8" sample in the closed system in which  $H_2O_2$  is used to trap the volatiles (Figure 12) resulted in finding a total of 5 ppm. Fe in the  $N_2O_4$  sample. While only this one experiment has been performed to date, these results strongly indicate volatile Fe species present in the  $N_2O_4$ . No other metals were looked for at the time because of lack of sufficient hydrolyzate.



FIGURE 12  
"CLOSED" HYDROLYSIS SET-UP



5) Direct Analysis of Fe by Aspiration of the Sample

An attempt was made to analyze for iron by direct aspiration of samples into the atomic absorption flame. By approximating a correction factor based on the known effects of viscosity (see Table 11) values of 0.68 ppm. Fe was found for "G8"  $N_2O_4$  and values of 0.41 and 0.43 ppm. Fe were found for "RR" respectively before and after exposure in a corrosion test cell.

Since these values approximate those found by evaporation and are in contrast with those found on closed hydrolyses, an independent measure of Fe content by a colorimetric method (7) (using a bathophenanthroline complex) in which the sample is hydrolyzed in aqueous HCl was tried. This procedure gave 4.5 and 8.5 ppm. Fe respectively for "RR" and "G8"  $N_2O_4$  from the storage tanks. Since this result checks with the closed hydrolysis result and comes close to what plant experience has noted in the past (8), we must currently view values obtained by direct aspiration with suspicion.

C. Conclusions and Recommendations

Emission Spectrographic and Atomic Absorption methods, working as a team are capable of identifying and quantitatively determining the trace metals present in  $N_2O_4$ .

The "G8"  $N_2O_4$ , as sampled from the storage tank, contains more iron than the "RR"  $N_2O_4$  (0.83 ppm. vs. 0.31 ppm.). The "RR"  $N_2O_4$  reacted as expected with the (6% Al, 4% V) titanium alloy used in the stress-corrosion test. Atomic Absorption analysis gave

results of 0.42 ppm. Al, 9.0 ppm. V, and 25.5 ppm. Ti in the "red"  $N_2O_4$  after the test. These results are not proportional to the metals as present in the titanium alloy, suggesting selective corrosion.

The "green" passive  $N_2O_4$  did not indicate any evidence of corrosion during the stress-corrosion test, as Al, V and Ti were not detected.

#### D. Future Work

All future analysis will be made by both open and closed systems of sample preparation, until it is determined whether or not there are in fact volatile species of metals present in the  $N_2O_4$ .

Further work is desirable on the direct aspiration method of Atomic Absorption analysis. Add-back experiments should probably be the first step in an attempt to pinpoint discrepancies between the direct aspiration values and the closed hydrolysis values for iron.

#### E. Experimental Section

The following work was done prior to receiving the two one-ton cylinders of  $N_2O_4$  in October, 1967. A cylinder of Matheson  $N_2O_4$  was used as the material for determining optimum methods of sample preparation as well as to establish the parameters to be used for Emission Spectrographic and Atomic Absorption analysis.

1) N<sub>2</sub>O<sub>4</sub>-Vaporization Method of Sample Preparation

Approximately 60 grams of Matheson N<sub>2</sub>O<sub>4</sub> was weighed into a tared 200 ml. platinum dish. While the sample was being transferred from the cylinder, the platinum dish was cooled by partial immersion in an ice bath. The N<sub>2</sub>O<sub>4</sub> was permitted to slowly volatilize while cooling, until the volume had been reduced to about 5 ml. Distilled water was added to the residual 5 ml. and the resulting solution taken almost to dryness on a low temperature hot plate. Distilled water was used to make a final volume of 10 ml.

2) N<sub>2</sub>O<sub>4</sub>-Hydrolysis Method of Sample Preparation

Forty ml. (ca. 60 grams) of N<sub>2</sub>O<sub>4</sub> was transferred from the cylinder into a 100 ml. graduate. The N<sub>2</sub>O<sub>4</sub> was hydrolyzed by slowly pouring it into an ice cooled 250 ml. Erlenmeyer flask containing 100 ml. of distilled water. This mixture was gently swirled while ice cooled, until there were no visible signs of activity and the mixture appeared to be homogeneous. The contents of the Erlenmeyer were transferred to a 200 ml. platinum dish and taken almost to dryness on a low temperature hot plate. Distilled water was used to make a final volume of 10 ml.

3) Conditions Used in Emission Spectrographic Analysis

Spectrograph - Bausch & Lomb Large Littrow

Optics Setting - Position 5 Quartz  
Slit ca. 30 mμ  
Sector Dish - 18.75% T

Source - Jarrell-Ash Varisource

Excitation - 5 sec. 4 amps, D.C. plus 85 sec. at 12 amps D.C.

Electrodes - Lower - 1/4" National L 3809 AGKSP drilled 2 mm. deep, 4 mm. dia., pierced 7 sec. at 12 amps D.C.

Upper - Ultra Carbon - Type 105 $\mu$

Photography - Kodak Spectrum Analysis No. 1  
Standard Development procedure using JA 3410 photoprocessor.

Sample & Standards Preparation - Tufts of C.P. cotton linters (metals free) were placed in each lower electrode cavity. The electrode was heated carefully by a gas-oxygen torch while the sample (0.1 and 1.0 ml.) and standard solutions (0.1 ml.) were pipetted and dried onto the linters. After drying, the linters were charred using minimum heating (prob. <400°C.) after which C.P. powdered graphite was placed on top to prevent sample loss during arcing and recording of the spectra.

Standards - A series of standards previously prepared were used for this analysis. They contain Mg, Ca and Al from 10 to 1280 ppm.; Pb, Cu, Cr, Ni and Fe from 1 to 128 ppm.; and Mn 0.1 to 12.8 ppm. Each standard contains twice the metals concentration of the next lowest.

#### 4) Atomic Absorption Analysis

Reagents - All chemicals used for this work were reagent grade. All standard solutions were prepared as outlined in Perkin-Elmer's "Analytical Methods for Atomic Absorption Spectrophotometry".

Apparatus - Perkin-Elmer, Model 303, Atomic Absorption Spectrophotometer. This instrument is fully described in the Perkin-Elmer literature. The Belling burner is used with air-acetylene mixtures. The N<sub>2</sub>O burner is used with N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> mixtures for analysis of refractory metals.

Instrumental Parameters - The instrumental parameters for each metal are fully described in the Perkin-Elmer "Analytical Methods for Atomic Absorption Spectrophotometry".

Table 8

Metals in Matheson N<sub>2</sub>O<sub>4</sub> Comparison  
Of Controlled Evaporation and "Open" Hydrolysis

	Emission Spectrographic (Semiquant.)		Atomic Absorption	
	Evaporated (ppm.)	Open Hydrolysis (ppm.)	Evaporated (ppm.)	Open Hydrolysis (ppm.)
Mg	<0.2	<0.2	*	*
Mn	0.02	0.03	<0.04	<0.04
Pb	0.1	0.2	<0.1	<0.1
Si	0.2	0.4	-	-
Fe	2	2	1.9	2.1
Cr	<<0.02	0.1	<0.1	0.25 (est.)
Ni	0.1	0.3	<0.1	0.3 (est.)
Al	0.1	0.3	*	*
Ti	<<0.1	<<0.1	*	*
Ca	<<0.2	<0.2	<0.04	0.1 (est.)
Cu	0.03	0.03	<0.1	<0.1
Zn	<<0.6	<<0.6	0.08	0.1
Ag	0.02	<0.01	<<0.25	<<0.25
Na	<<2	<<2	0.09	0.42
Sn	<<0.1	<<0.1	<<0.25	<<0.25
Bi	<<0.1	<<0.1	**	**
Sb	<<0.1	<<0.1	**	**
Cd	<<0.1	<<0.1	**	**
B	<<0.1	0.5	-	-
V	<<0.1	<<0.1	*	*
Co	<<0.1	<<0.1	**	**
Mo	<<0.1	<<0.1	-	-
K	<<20	<<20	<0.04	0.12

< = Less than but detected.

<< = Less than and not detected.

\* = Hollow cathode tubes were not available, but have now been purchased to permit the analysis of these metals.

\*\* = Hollow cathode tubes were available for the analysis of these metals but there was insufficient sample solutions.

5) Analysis of "RR" and "G8" N<sub>2</sub>O<sub>4</sub>

After receipt of the two one-ton tanks of N<sub>2</sub>O<sub>4</sub> the first step was to determine metallic differences, if any, between "red" reactive and "green" passive N<sub>2</sub>O<sub>4</sub>.

Samples of both "red" and "green" N<sub>2</sub>O<sub>4</sub> were collected and prepared for analysis by evaporation and hydrolyses on five consecutive working days.

Two 50-ml. sampling flasks with Fisher-Porter valves were cleaned successively with HNO<sub>3</sub>, H<sub>2</sub>O, and acetone after which they were thoroughly dried.

Two 200-ml. platinum dishes were steeped in hot HNO<sub>3</sub> for two hours, thoroughly rinsed with distilled water, and dried by heating on hot plate.

After collecting the samples, the sampling flask was weighed and the total contents poured into the ice-cooled platinum dishes. The same procedures were followed as before except that the sample was reduced to a 5 ml. final volume in order to increase the sensitivity of the method.

	<u>Grams of N<sub>2</sub>O<sub>4</sub></u>					
	<u>11/27/67</u>	<u>11/28/67</u>	<u>11/29/67</u>	<u>11/30/67</u>	<u>12/1/67</u>	<u>Average</u>
"Green" (A-2)	76.0	74.5	80.8	76.7	79.4	77.5
"Red" (A-7)	81.2	89.3	89.0	89.6	85.3	88.1

It was discovered that a "scum" appeared on the surface of the "red" N<sub>2</sub>O<sub>4</sub> during evaporation.

### Spectrographic Analysis

Visual inspection of this emission spectrographic plate indicates that the only metallic difference between the "red" and "green"  $N_2O_4$  was iron, more being present in the "green".

### Atomic Absorption Analysis

Table 9

#### Metals in Hercules $N_2O_4$ by Atomic Absorption

		<u>G8</u> <u>(ppm.)</u>	<u>Av.</u>	<u>Std.Av.</u>	<u>RR</u> <u>(ppm.)</u>	<u>Av.</u>	<u>Std.Av.</u>
Fe	11/27	0.93	0.83	0.078	0.33	0.31	0.013
	11/28	0.88			0.32		
	11/29	0.79			0.30		
	11/30	0.81			0.31		
	12/1	0.73			0.30		
Na			0.02			0.02	
K			0.02			0.02	
Zn			0.02			0.02	
Ca			0.02			0.006	
Pb			0.05			0.04	

#### Analysis of G8 and RR $N_2O_4$ After Titanium Alloy (6Al-4V) Stress Corrosion Testing

##### 6) Emission Spectrograph

It was observed that "RR"  $N_2O_4$  after the test contained Ti and V which were not present in the "G8" sample. Both green and red  $N_2O_4$  seemed to slightly increase in iron content during the corrosion test. No other metallic differences were observed.



Table 10  
Metals in  $N_2O_4$  by Atomic Absorption  
After Corrosion Test

	<u>"Green"</u>		<u>"Red"</u>	
	<u>Before (ppm.)</u>	<u>After (ppm.)</u>	<u>Before (ppm.)</u>	<u>After (ppm.)</u>
Fe	1.1	1.6	0.33	1.3
Cr	<0.03	<0.03	<0.03	0.03 (est.)
Ni	<0.03	<0.03	<0.03	<0.03
Al	<0.03	<0.03	<0.03	0.42
Ti	<0.65	<0.65	<0.65	25.5
V	<0.13	<0.13	<0.13	9.0

Note: The Before and After refers to before and after the corrosion tests.

#### 7) "Closed" System for Hydrolyses of $N_2O_4$

Using the apparatus sketched in Figure 12, chilled "green"  $N_2O_4$  was poured into the burette and 5 ml. allowed to enter below the surface of the cold distilled water. The burette was then removed and an unpierced rubber Sani-Tab Cap was snapped over the mouth of the nitration flask. Initially the  $N_2O_4$  turned blue and laid passively on the bottom of the flask. The flask was gently swirled in the ice-bath until the  $N_2O_4$  was mixed with the water. The off gasses from the resultant blue solution were bubbled through an aqueous  $H_2O_2$  solution and collected in a 100-ml. graduate. After the initial reaction in the ice-bath the flask was

brought slowly to room temperature, still swirling, and then finally placed on steam bath. At all times the off gasses were passed into the  $\text{H}_2\text{O}_2\text{-H}_2\text{O}$  solution.

As the flask was being brought to room temperature more than 100 ml. of gas had been collected.

The contents of the hydrolysis flask were poured into a 200-ml. platinum dish and taken almost to dryness on hot plate, then made to a 5 ml. final volume.

The 400 ml.  $\text{H}_2\text{O}_2\text{-H}_2\text{O}$  solution in the beaker was placed on a hot plate and reduced to about 75 ml., after which this solution was transferred to a 200-ml. platinum dish, taken almost to dryness and made up to a final 5 ml. volume.

Both solutions were analyzed by atomic absorption using standard techniques described previously. On the basis of the original  $\text{N}_2\text{O}_4$  (5 ml. = 7.5 g.), the hydrolysis fraction contained 4 ppm. Fe and the off gasses 1 ppm. Fe.

#### 8) Direct Analysis of $\text{N}_2\text{O}_4$ by Atomic Absorption

This analysis was made to check the possibility of the direct analysis of  $\text{N}_2\text{O}_4$  without any sample preparation whatsoever.

The atomizer assembly was placed in the Perkin-Elmer Atomic Absorption Spectrophotometer. Chilled  $\text{N}_2\text{O}_4$  samples were poured into prechilled 20 x 150 mm. test tubes and aspirated directly from the tubes into the atomizer chamber.

Table 11  
Data on Direct Aspiration of N<sub>2</sub>O<sub>4</sub>  
Into Atomic Absorption Spectrometer

	<u>%A</u>	<u>Abs.</u>	<u>ppm. Fe</u>		
			<u>Uncorrected</u>	<u>x f</u>	<u>= Corrected</u>
"Green" N <sub>2</sub> O <sub>4</sub> (Tank, 1/5/68)	18.3	0878	2.5	0.27	0.68
"Red" N <sub>2</sub> O <sub>4</sub> (Tank, 1/5/68)	12.1	0560	1.5	0.27	0.41
"Red" N <sub>2</sub> O <sub>4</sub> (Corrosion cell 1/5/68)	2.5	0580	1.6	0.27	0.43
Fe standard 10 (1% HCl Aqueous Soln.)	46.0	2676	10		
Fe standard 5 (1% HCl Aqueous Soln.)	29.4	1512	5		
Fe standard 2.5 (1% HCl Aqueous Soln.)	18.0	0862	2.5		
Fe standard 1.0 (1% HCl Aqueous Soln.)	9.3	0424	1.0		

The N<sub>2</sub>O<sub>4</sub> correction factor which is on approximation was calculated as follows:

$$\begin{aligned}
 f &= \frac{\text{Viscosity N}_2\text{O}_4}{\text{Viscosity H}_2\text{O}} \times \frac{\text{Density H}_2\text{O}}{\text{Density N}_2\text{O}_4} \\
 &= \frac{0.4}{1} \times \frac{1}{1.5} \\
 &= 0.27
 \end{aligned}$$

No correction factor was applied that takes into consideration the change in absorbance due to the effect of N<sub>2</sub>O<sub>4</sub> on the flame characteristics.

## VI. Determination of Chlorine by X-ray Emission

### A. Introduction

Any chlorine that may be present in  $\text{N}_2\text{O}_4$  is expected to be in the form of  $\text{NOCl}$ . This hydrolyzes rapidly in the presence of water, and the addition of a relatively small volume of  $\text{AgNO}_3$  converts the chlorine to  $\text{AgCl}$ . Previous work indicated that the filtration of the  $\text{AgCl}$  on Millipore filters and reading the chloride present by x-ray emission had the required sensitivity but based upon the 95% confidence level of counting statistics, the expected level of precision was not attained. However, by substituting a smaller size Millipore filter (25 mm.) for the larger one (47 mm.) and by implementing certain changes in the conditions of precipitation excellent precision was obtained.

### B. Discussion of Results

#### 1) Apparatus and Sampling Procedures

The substitution of the smaller 25 mm. Millipore filter for the 47 mm. size has resulted in a five-fold increase in sensitivity. To obtain better precision the following procedural changes were made: 1) to reduce the decomposition effect of light, the precipitation of  $\text{AgCl}$  is carried out in dark flasks, 2) the precipitate is cooled to  $0^\circ\text{C}$ . in ice before filtering, 3) a final wash of the precipitate with isopropanol removes the  $\text{AgCl}$  that cannot be washed from the sides of the filter holder with water due to its surface tension.

## 2) Precision

A study of the precision was made to determine the limitations of the method. Using the procedure described in the Experimental Section, five 2-ml. aliquots of both "RR" and "G8"  $N_2O_4$  were hydrolyzed and the chloride content determined using x-ray emission. A summary of the data is found in Tables 12 to 15. The precision of the method of standard preparation was also checked (Table 16). The counting precision for the rotation mode was established by making five replicate counts on a typical sample. Each of the values found in Table 17 representing a complete counting determination (after each count the sample was removed then reinstalled).

It is apparent from these data that the major limitation of the precision is the placement of the sample in the specimen holder.

## 3) Sensitivity

Using the  $K\alpha Cl$  line and based upon a 7.5 g. sample of  $N_2O_4$  and the number of counts equal to 2 times the net counts of a reagent blank, 0.5 ppm. chlorine can be easily detected. By counting on the  $L\alpha Ag$  line a value representing 0.3 ppm. Cl can be obtained. However, due to the possibility of a reaction between the silver and various impurities in the  $N_2O_4$  counting at the  $L\alpha Ag$  line was discontinued.

## 4) Chloride Content in $N_2O_4$

The ppm. chloride present in the particular "RR" and "G8" samples of  $N_2O_4$  are found in Tables 12 to 15. Both samples contain approximately 15 ppm. Cl. Since their ranges overlap, there appears

to be no significant differences in chloride content of the "RR" and "G8"  $N_2O_4$ .

Particulate matter was observed to be present after hydrolysis. To check the effect of the particulate matter on the chloride content, the hydrolyzates were filtered after neutralization with  $NH_4OH$ . Qualitative Emission Spectrographic Analysis of these base insolubles are as follows:

Major = Ag, Si  
Minor = Mg, Fe, Al, Ca  
Trace = B, Mn, Pb, Cr, Ni, Ti, Cu

The usual precipitation procedure was followed afterwards. Data on Tables 2 and 3B shows that the chloride content obtained after filtration is slightly higher than if no attempt to remove the particulate matter is made.

To check whether any chloride is present as an acid soluble base insoluble entity, a sample of  $N_2O_4$  was hydrolyzed in water containing no  $AgNO_3$ , then neutralized and filtered. Counting the Millipore filter containing the  $NH_4OH$  insoluble matter yield a chloride content of 0 ppm.

To check possible contamination from the glassware, samples of "RR" and "G8"  $N_2O_4$  were collected in stainless steel vessels and the hydrolysis procedure was carried out in platinum dishes. Duplicate determinations yielded 12.3 and 13.6 ppm. chlorine in the "RR" and 14.5 and 12.3 ppm. Cl for the "G8". However, since the sample weights are probably high (sample weight obtained by

difference in steel vessel weights where some  $N_2O_4$  was lost during sample transfer) no significant Cl contamination from the glass exists. However, all glassware should be boiled in hot  $HNO_3$  before use.

C. Future Work

In the next quarter an attempt will be made to check the accuracy of the method (by add-back experiments of  $NOCl$ ) in the 10 to 20 ppm. Cl range.

D. Experimental

1) Apparatus and Reagents

(1) X-ray emission spectrometer - General Electric XRD6 equipped with a chromium target tube, a pentaerythritol crystal, and a sample spinner.

(2) A Millipore filtering apparatus consisting of:

a) Pyrex filter holder

b) Filler flask

c) Filters - Type GS, 25 mm. diameter and a pore size of  $0.22\mu$

(3) Black 125 ml. Erlenmeyer flasks - prepared by spraying the outside of the flasks with black paint, but leaving a spot on the bottom ( $\sim 1$ " diameter) free of paint which is used to observe indicator color changes.

(4) Distilled water - chloride free.

(5) Nitric acid - 1:1 by volume.

(6) Silver nitrate - 5% aqueous solution.

- (7) Ammonium hydroxide - 1:1 by volume.
- (8) Potassium chloride - Analytical reagent grade, dried for 1 hour at 105°C. and stored in a dessicator.
- (9) Isopropanol - Chloride free analytical reagent grade filtered through 22 $\mu$  Millipore if necessary to remove any particulate matter.

## 2) Preparation of Standards

A chloride stock solution was prepared by accurately weighing 0.210 g. of dried KCl and made to volume in a one-liter volumetric. A chloride standard solution containing 10  $\mu$ g. Cl/ml. was made by pipetting 25 ml. of the stock solution into a 250-ml. volumetric and making up to volume with chloride free distilled water.

## 3) Calibration

A series of standards were prepared by pipetting 3, 4, 5, 6, 8 and 10 ml. of the chloride standard solution into the black 125-ml. Erlenmeyer flasks. To this was added 5 ml. of 5% AgNO<sub>3</sub> and 3 ml. 1:1 HNO<sub>3</sub>. Then the solution was neutralized to the phenolphthalein endpoint with 1:1 NH<sub>4</sub>OH. The solution was acidified with 1 ml. of 1:1 HNO<sub>3</sub>, allowed to stand for 5 minutes, then cooled in ice to 0°C. The solution was transferred to the filter holder and filtered under vacuum. It was sucked dry and washed with two 10-ml. portions of cooled distilled water acidified with 1 drop of concentrated HNO<sub>3</sub>. A final rinse of the sides of the filter holder was made with 2 ml. of cooled isopropanol to wash down any AgCl



precipitate which adhered to the filter holder. The filter was covered with a 50 ml. black-painted beaker and air dried. The dried filter is mounted as shown in (Figure 15) and placed in the sample spinner. The total counts at the  $2\theta$  angle and the background angle were obtained using the instrument parameters listed below.

Path - helium

Counting time - 100 sec.

Target - chromium

X-ray power - 37 ma, 55 KV at constant potential

Crystal - pentaerythritol

$2\theta$  angle -  $65.49^\circ$

Background angle -  $67.49^\circ$

From the net counts (counts at the  $2\theta$  angle minus background counts) the intensity ratio of each standard compared to the most concentrated standard was determined. From this a plot of intensity ratio vs.  $\mu\text{g. Cl}$  (Figure 13 and 14) was made.

#### 4) Procedure

Five ml. of 5%  $\text{AgNO}_3$  was pipetted into a 50-ml. Erlenmeyer and cooled in an ice bath. Using a chilled pipet, 2-5 ml. of cold ( $0^\circ\text{C.}$ )  $\text{N}_2\text{O}_4$  was added slowly into the flask without mixing. The sample size was selected to contain between 20-50  $\mu\text{g. of Cl}$ . The flask was allowed to remain in the icebath undisturbed until the two layers become one. It was removed from the ice and allowed to warm to room temperature. By use of a slow stream of nitrogen and swirling the majority of the brown fumes were removed.

FIGURE 13

C1 LEVEL VS. COUNTING INTENSITY RATIO  
EXTENDED RANGE

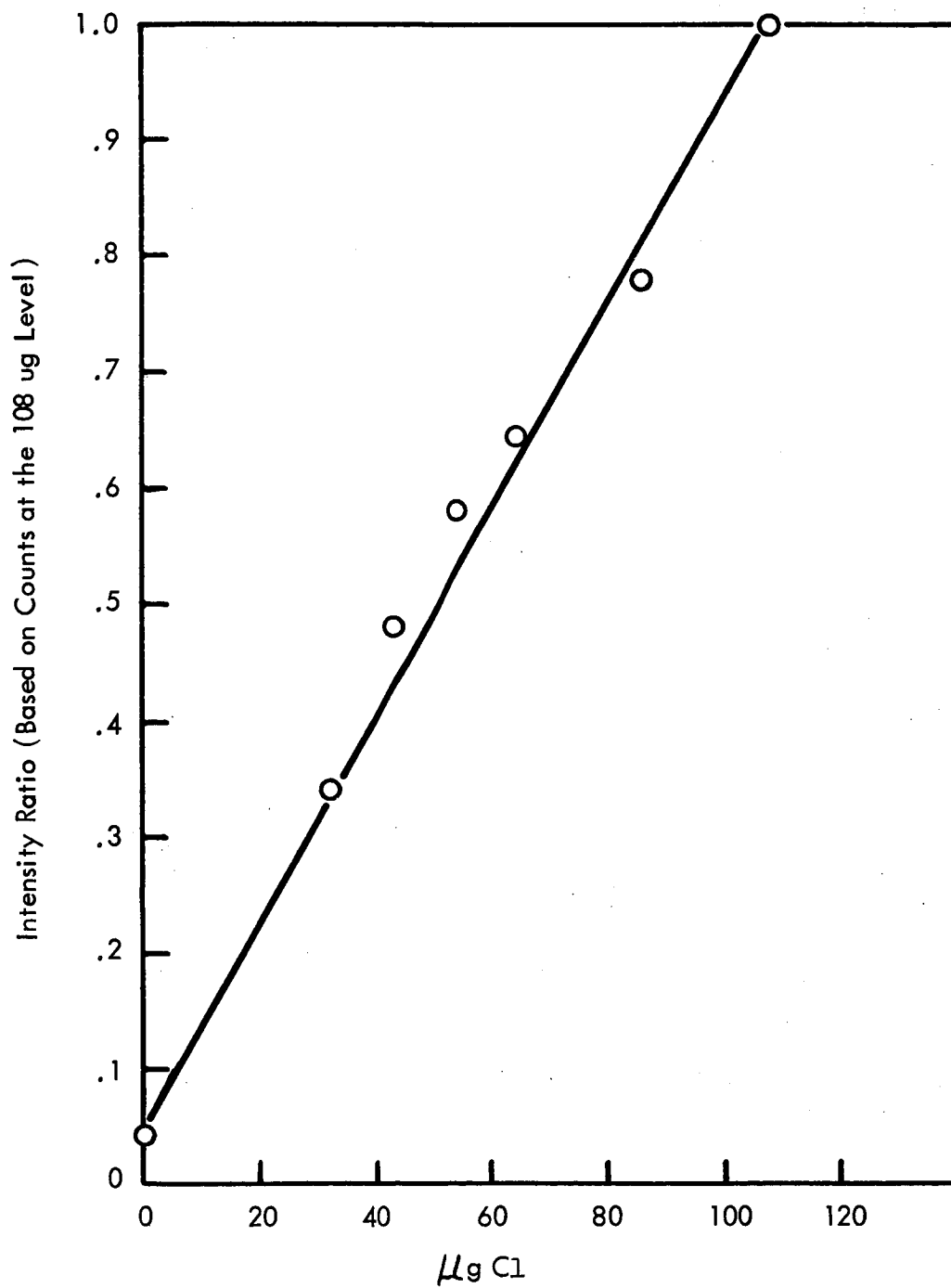


FIGURE 14

Cl LEVEL VS. COUNTING INTENSITY RATIO  
WORKING CURVE

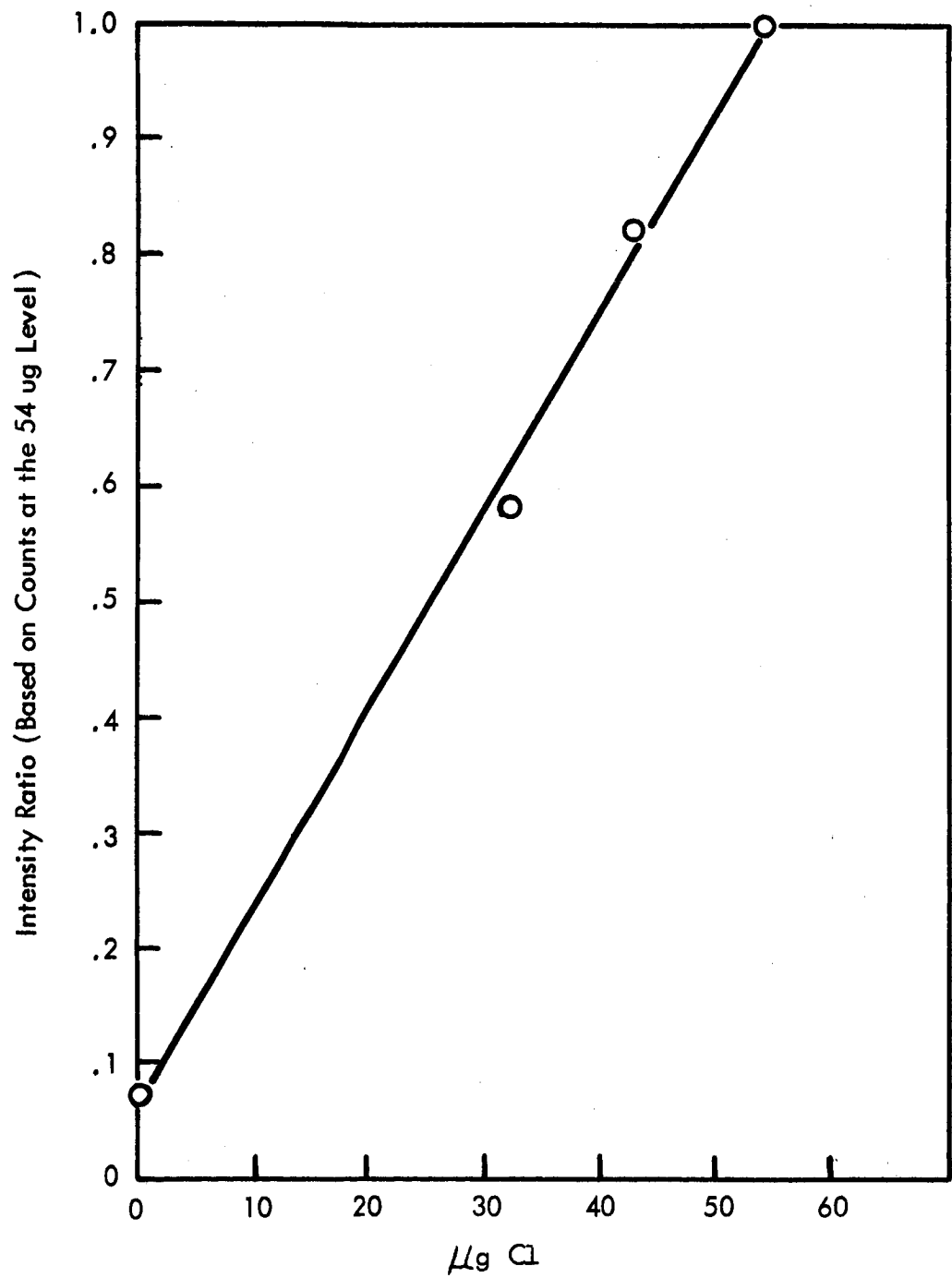
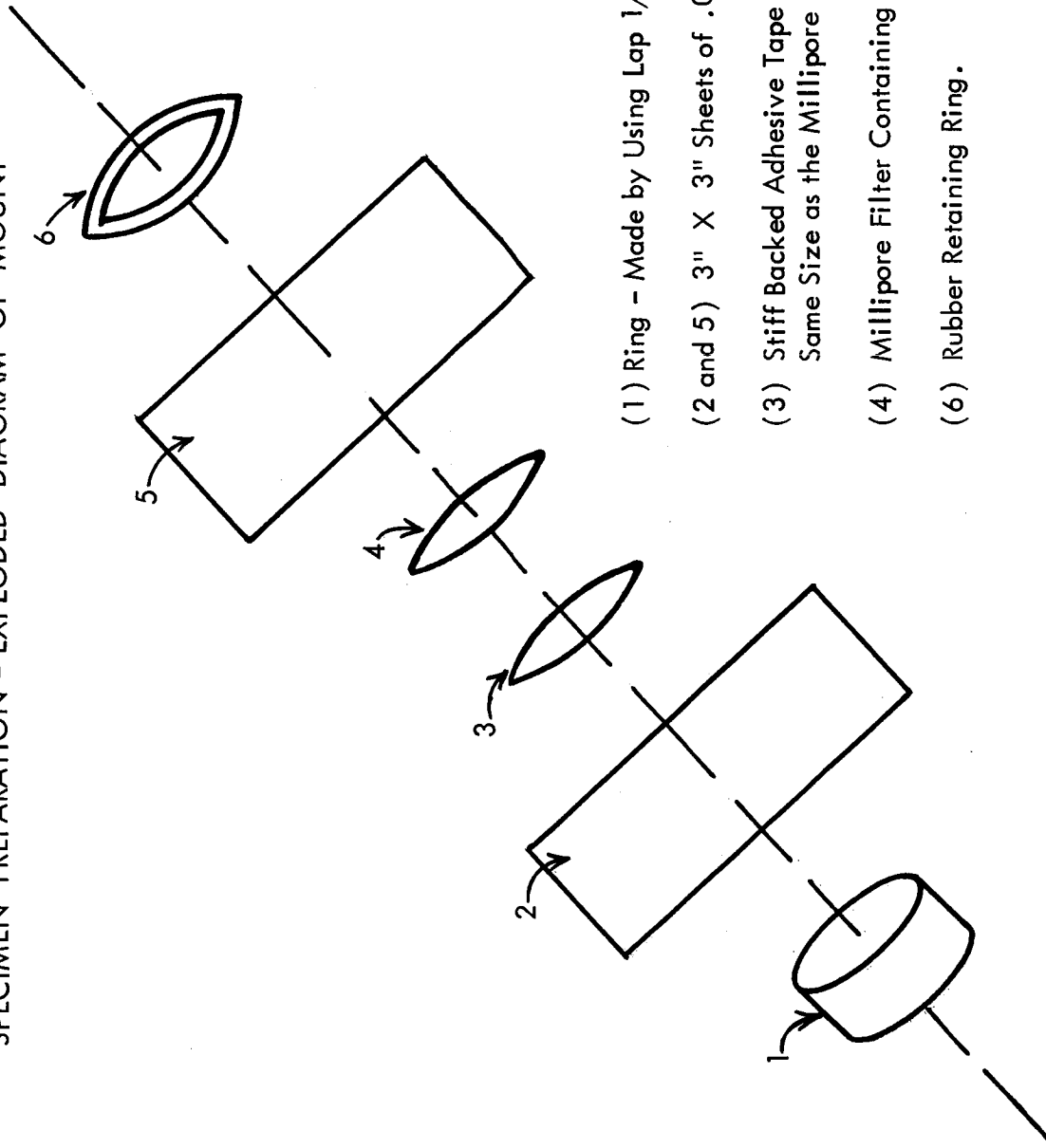


FIGURE 15

SPECIMEN PREPARATION - EXPLODED DIAGRAM OF MOUNT



(1) Ring - Made by Using Lap 1/2" Cut from a Spex Liquid Cell .

(2 and 5) 3" X 3" Sheets of .00025" Spex X-ray Film.

(3) Stiff Backed Adhesive Tape (Chloride Free) Cut to the Same Size as the Millipore Filter.

(4) Millipore Filter Containing the Ag Cl Precipitate.

(6) Rubber Retaining Ring.

Complete removal of the brown fumes is accomplished by placing the flask on a steam bath. When the solution is clear and colorless, it was transferred to a black 125-ml. Erlenmeyer flask with the aid of a little chloride free distilled water, and neutralized with 1:1  $\text{NH}_4\text{OH}$  to the phenolphthalein endpoint. After acidification with 1:1  $\text{HNO}_3$ , it was allowed to stand at room temperature for 5 minutes, then cooled in ice before filtering. The intensity ratio was determined as described under calibration. The micrograms of chloride present was obtained from the calibration curve.

5) Calculation

The parts per million chloride in  $\text{N}_2\text{O}_4$  is calculated using the following equation.

$$\frac{\text{micrograms chloride}}{\text{ml. N}_2\text{O}_4 \times 1.5} = \text{ppm. chloride}$$

$$\text{ppm. Cl} \times 1.85 = \text{ppm. NOCl}$$

Table 12

(Precision Study on "RR"  $N_2O_4$  (Not Filtered at a pH >7)  
54  $\mu g. Cl^-$  Standard Used  $I_0 = 133340$  Counts

<u>2 <math>\theta</math> Angle</u>	<u>Background Angle</u>	<u>Net</u>	<u>I/<math>I_0</math></u>	<u>(a) <math>\mu g. Cl</math></u>	<u>(b) ppm. Cl</u>
125650	1160	124490	.934	50.2	16.7
116270	1100	115170	.864	46.1	15.4
115190	1070	114120	.856	45.6	15.2
125710	1190	124520	.934	50.2	16.7
117440	1030	116360	.873	46.6	15.5

$$\begin{aligned} \text{Av.} &= 15.9 \pm .65 \\ S &= .75 \\ \text{Sr} &= 4.7\% \end{aligned}$$

(a)  $\mu g. Cl$  obtained from calibration curve in Figure 14.

(b) based on a 2 ml.  $N_2O_4$  sample and a density of 1.5.

Table 13

Precision Study on "RR"  $N_2O_4$  (Filtered at a pH >7)  
54  $\mu g. Cl$  Standard Used  $I_0 = 137800$  Counts

<u>2 <math>\theta</math> Angle</u>	<u>Background Angle</u>	<u>Net</u>	<u>I/<math>I_0</math></u>	<u>(a) <math>\mu g. Cl</math></u>	<u>(b) ppm. Cl</u>
132280	1350	130930	.950	51.1	17.0
151920	1470	150450	1.092	59.3	19.8
139510	1380	138130	1.002	54.1	18.0
133450	1450	132000	.958	51.6	17.2
141120	1440	139680	1.014	54.8	18.3

$$\begin{aligned} \text{Av.} &= 18.1 \pm .77 \\ S &= 1.1 \\ \text{Sr} &= 5.9\% \end{aligned}$$

(a)  $\mu g. Cl$  obtained from calibration curve in Figure 14.

(b) based on a 2 ml.  $N_2O_4$  and a density of 1.5.

Table 14

Precision Study on "G8" N<sub>2</sub>O<sub>4</sub> (Not Filtered at pH >7)  
54  $\mu$ g. Cl Standard Used I<sub>0</sub> = 139830 Counts

<u>2 <math>\theta</math> Angle</u>	<u>Background Angle</u>	<u>Net</u>	<u>I/I<sub>0</sub></u>	<u>(a) <math>\mu</math>g. Cl</u>	<u>(b) ppm. Cl</u>
120330	1450	119880	.857	45.7	15.2
113870	1450	112420	.803	42.6	14.2
117760	1500	116260	.831	44.2	14.7
111890	1360	110530	.790	41.8	13.9
116310	1430	114880	.822	43.7	14.6

$$\text{Av.} = 14.5 \pm 37$$

$$S = .50$$

$$Sr = 3.4\%$$

(a)  $\mu$ g. Cl obtained from calibration curve in Figure 14.

(b) Based on a 2 ml. N<sub>2</sub>O<sub>4</sub> sample and a density of 1.5.

Table 15

Precision Study on "G8" N<sub>2</sub>O<sub>4</sub> (filtered at pH >7)  
54  $\mu$ g. Cl Standard I<sub>0</sub> = 139400 Counts

<u>2 <math>\theta</math> Angle</u>	<u>Background Angle</u>	<u>Net</u>	<u>I/I<sub>0</sub></u>	<u>(a) <math>\mu</math>g. Cl</u>	<u>(b) ppm. Cl</u>
120330	1470	127140	.912	48.9	16.3
128270	1600	126670	.909	48.7	16.2
127750	1530	126220	.905	48.5	16.2
132070	1590	130480	.936	50.3	16.8
126710	1600	125110	.897	48.0	16.0

$$\text{Av.} = 16.3 \pm .19$$

$$S = .28$$

$$Sr = 1.7\%$$

(a)  $\mu$ g. Cl obtained from calibration curve Figure 14.

(b) Based on a 2 ml. N<sub>2</sub>O<sub>4</sub> sample and a density of 1.5.

Table 16

Precision Study on Method of Standard Preparation  
5.0 ml. of 10.8  $\mu$ g./ml. Chloride Standard Used  
K $\alpha$  Chlorine Line

<u>* 2 <math>\theta</math> Angle</u>	<u>* Background Angle</u>	<u>Net</u>	<u>d</u>
136500	1510	135020	2494
142150	1530	140620	3106
137740	1560	136180	1334
135130	1460	134670	2844
142670	1590	141080	3566

Av. = 137514 2670

S = 3100

Sr = 2.3%

\* A counting time of 100 sec. on rotated samples used.

Table 17

Counting Precision on a Typical Sample(a)  
54  $\mu$ g. Standard Used I<sub>0</sub> = 142610

<u>2 <math>\theta</math> Angle</u>	<u>Background Angle</u>	<u>Net</u>	<u>I/I<sub>0</sub></u>	<u>(b) <math>\mu</math>g. Cl</u>	<u>(c) ppm. Cl</u>
126890	2530	124360	.872	46.6	15.5
127270	2880	124390	.872	46.6	15.5
128300	2870	125430	.880	47.0	15.7
119560	2660	116900	.829	43.6	14.5
120360	2180	118180	.829	44.1	14.7

Av. = 15.2  $\pm$  .47

S = .54

Sr = 3.6%

(a) "G8" N<sub>2</sub>O<sub>4</sub> used.

(b)  $\mu$ g. Cl obtained from calibration curve Figure 14.

(c) Use of a 2-ml. sample and a density of 1.5.

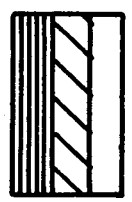
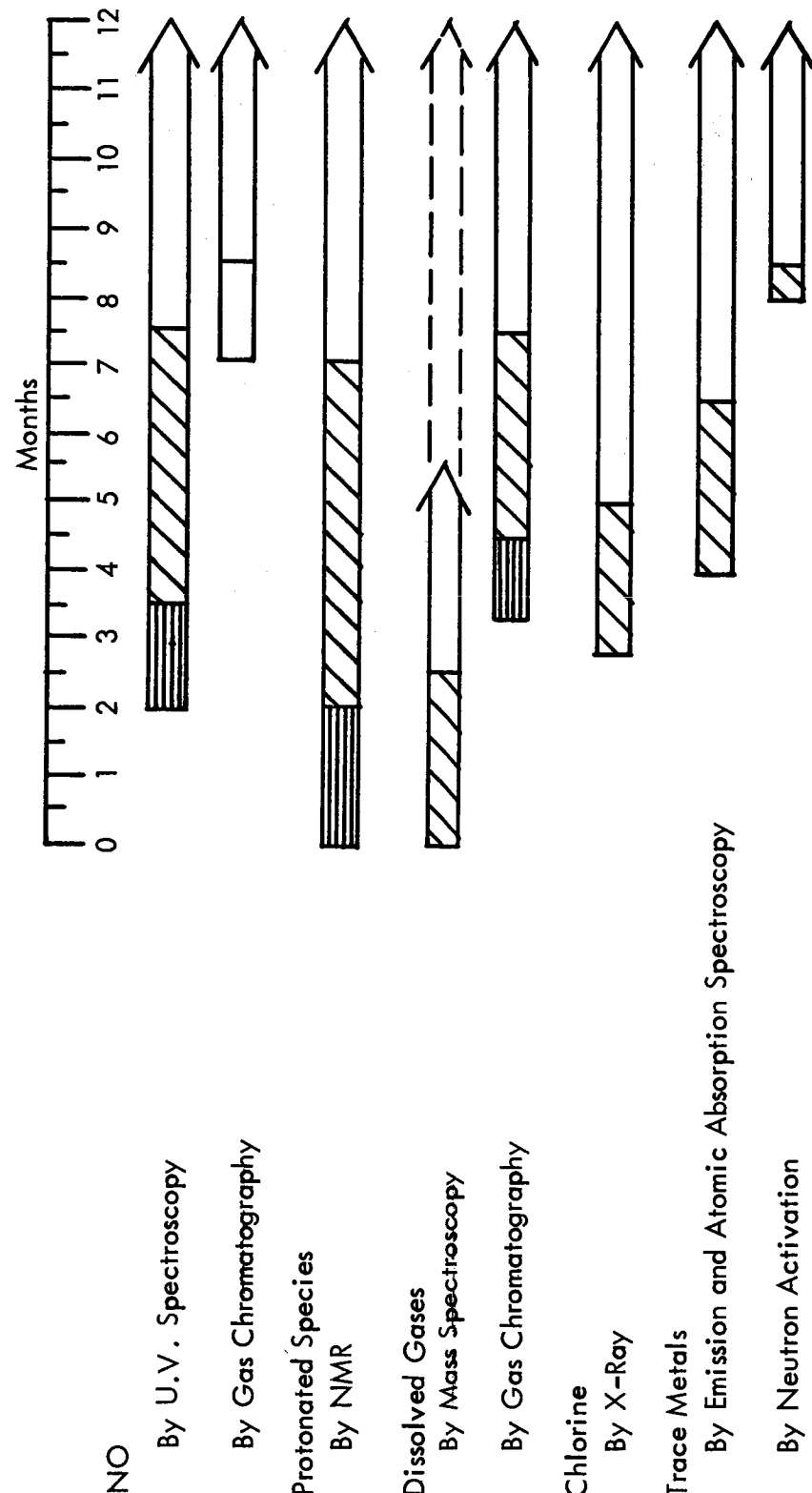


VII. Revised Schedule of Analytical Effort

A revised outline of the anticipated schedule for characterization of  $\text{N}_2\text{O}_4$  samples is given in Figure 16.

FIGURE 16

PHASE B CHARACTERIZATION OF PROPELLANT  $N_2O_4$  - REVISED SCHEDULE



Equipment Purchase and Modification  
Calibration Development, and Prove-In  
Correlation Study

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